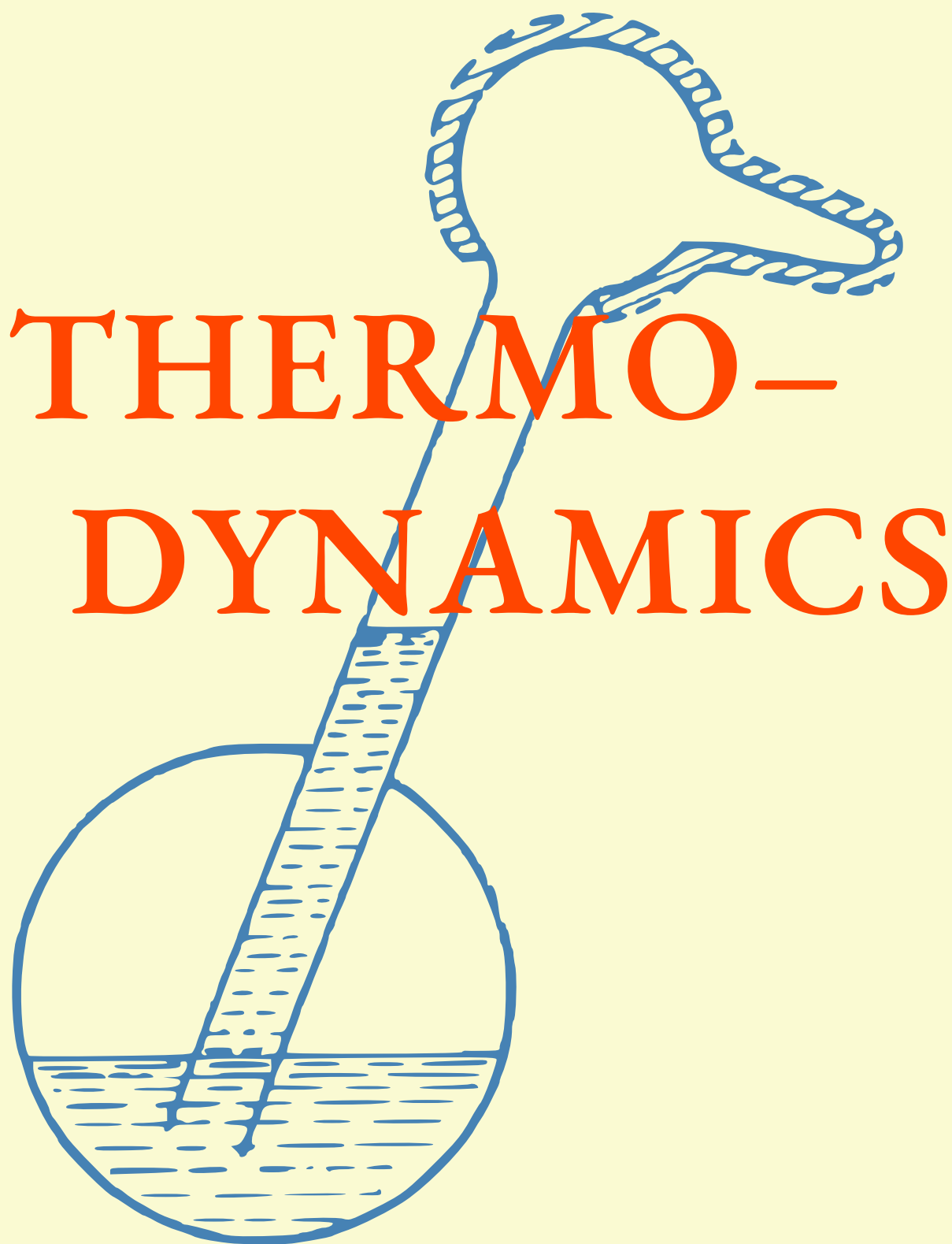


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THERMODYNAMICS

Thermodynamics

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PREFACE

THIS book is the first part of a course on "Thermodynamics and Statistical Physics" held at present in physical and physicomathematical faculties of our universities. In comparison with existing courses of thermodynamics the book has the following distinctive features:

1. Greater attention than in other books is devoted to a discussion of the initial propositions of thermodynamics, which enables us to establish both the limitations of thermodynamics and its organic connexion with statistical physics.

2. The content of the second law of thermodynamics is analysed logically and with greater consistency, by taking into account the existence of negative absolute temperatures.

3. The methods of thermodynamics are considered and discussed in detail.

4. The theory of critical phenomena is expounded according to Gibbs, which enables us to establish the connexion of these phenomena with phase transitions of the second kind.

5. The thermodynamics of systems with negative absolute temperatures is treated.

6. The fundamentals of the thermodynamics of irreversible processes are given.

7. The large number of problems included in the book form an integral part of the course. Many are devoted to certain additional questions that are not always treated in the course and do not enter in the main text of the book. For these reasons the solutions of the problems are set out in as much detail as possible.

The author considers it his duty to express here his gratitude to Academician N. N. Bogolyubov and Prof. A. A. Vlasov for their comments on various questions of thermodynamics and statistical physics, as well as to the members of the methodological seminar of the physical faculty of Moscow State University for discussing at this seminar methodological problems arising in connection with the book.

I. P. BAZAROV

INTRODUCTION

THE SEQUENCE of the various courses of both general and theoretical physics is determined by the gradual transition to the study of more and more complex forms of *motion* of matter.

Mechanics studies the laws of displacement, the simplest form of *motion* of matter. Thermodynamics and statistical physics consider phenomena caused by the combined action of a very large number of continually moving molecules or other particles, of which the bodies surrounding us consist. Owing to the large number of particles their disorderly motion acquires new qualities. We have here an example of dialectic transition of quantity into quality when the increase of the number of mechanically moving particles in a body gives rise to a qualitatively new type of motion, namely thermal motion.†

Thermodynamics and statistical physics study the thermal form of motion of matter with its own specific laws. This does not mean that either thermodynamics or statistical physics are sciences of the thermal phenomena; they study not only thermal phenomena but also electric, magnetic and other phenomena in bodies. The study of these phenomena, however, is carried out from the viewpoint of the specific properties of the thermal motion in them. The main contents of both thermodynamics and statistical physics consist in the analysis of the laws of thermal motion in systems that are found in thermal equilibrium‡ and in the passage of systems to a state of equilibrium. It can be seen from this that the object of the study of both thermodynamics and statistical physics is one and the

† "Motion is not only a change of position; in super-mechanical regions it is also a change of quality. The discovery that heat is a certain molecular motion opened up a new epoch in the history of science. However, if I had nothing else to say about heat except that it represents a certain displacement of molecules, I should better say nothing altogether" (F. Engels, *The Dialectics of Nature*, Gospolitizdat, 1952, page 201). This statement of Engels points out the fact that a qualitatively new form of motion—thermal motion—does not reduce [simply] to the mechanical motion of the separate particles.

‡ See § 1 for more details on thermal equilibrium.

same. Their essential difference from each other consists in the methods of investigation.

Whereas thermodynamics studies the general properties of physical systems in equilibrium by proceeding from two basic laws, called the laws of thermodynamics, together with a whole series of other experimental results, and does not explicitly use notions on the molecular structure of a substance, in the analysis of these properties statistical physics proceeds at its very beginning from molecular models of the structure of physical systems, by making wide use of the methods of the mathematical theory of probabilities.

The macroscopical approach of thermodynamics, i.e. its not being connected with the molecular-kinetic essence of the laws studied by it, leads on the one hand, to great and important results concerning the properties of physical systems, and, on the other hand, sets a limit to the depth to which these properties can be studied since it does not enable us to discover the nature of the phenomena studied. As a consequence of this, there has developed, alongside with thermodynamics, the molecular-kinetic theory of the properties of physical systems, and all the investigators whose names are connected with the development of thermodynamics have devoted great attention to the molecular-kinetic foundation of the results of thermodynamics.

Thermodynamics is a first mighty stride on the way to studying the laws in a large set of continuously moving and interacting particles (the so-called statistical laws); a detailed and more complete analysis of these laws requires the use of statistical methods.

Thermodynamics, however, must not be dismissed as part of the material of statistical physics. Though, in the end, all properties of physical systems are caused by the molecular motion in them, thermodynamics enables us to establish many of these properties without having recourse to notions of the molecular structure of bodies. The methods of thermodynamics are sufficient for solving very many practically important problems. All this, on the one hand, limits the scope of thermodynamics and, on the other hand, gives it a definite advantage in comparison with molecular theories.

There are no grounds today for drawing a sharp boundary between thermodynamics and statistical physics; nevertheless the definite advantage of thermodynamics and the specific nature of its methods make it important that a preliminary separate treatment of thermodynamics be given, making use of such *qualitative* molecular representations as are required.

The advantage of thermodynamics as compared with statistics consists in that it enables us by means of its principles to take into account easily laws observed experimentally and to obtain fundamental results from them. In just this manner was Nernst's heat theorem established in its time, the degeneracy of gases at low temperatures was predicted, the theory of phase transitions of the second kind was developed etc., while today the thermodynamic theory of kinetic phenomena in physical systems (the so-called thermodynamics of irreversible processes) is being successfully developed. The statistical theory of macroscopic processes lags in this respect behind thermodynamics. It can be seen from this that the treatment of thermodynamics as a separate, to a certain extent independent, subject is justified not only on pedagogical grounds.

Historically, thermodynamics† arose from the needs of heat engineering. The arising of thermodynamics was stimulated by the development of productive forces. The invention at the beginning of the nineteenth century of the steam-engine put before science the task of the theoretical investigation of the work of heat-engines with a view to increasing their efficiency. An investigation of this type was carried out in 1824 in the first work on thermodynamics by the French engineer and physicist Sadi Carnot and led him to establish theorems that determine the largest [possible] efficiency of heat-engines. These theorems later enabled one of the basic laws of thermodynamics—the second law, to be formulated. Somewhat later, in the forties of the nineteenth century, as a result of the investigations of Mayer, Joule, Helmholtz and others the mechanical equivalent of heat was established and, on this basis, the law of conservation and transformation of energy, called the first law of thermodynamics, was discovered.

As a formal scientific system proceeding from Carnot's work and from the law of conservation and transformation of energy, thermodynamics first occurred in the fifties of the past century in works of Clausius and Thomson-Kelvin, in which the modern formulations of the second law were given and the most important concepts of entropy and absolute temperature were introduced. The main method

† Thermodynamics means literally not the study of heat motion but the science of "motive power" arising in thermal processes. Thus the first work on thermodynamics was called "Reflections on the motive power of fire and on the machines capable of developing this power" (Sadi Carnot, 1824), in which the term "motive power" denotes the useful action (work) that an engine can provide at the expense of heat.

of investigation of thermodynamics in the nineteenth century was the method of closed-cycle processes.

Of exceptionally great importance for thermodynamics were Gibbs's works published at the end of the nineteenth century. In them a new method of thermodynamic investigations, the method of thermodynamic potentials, was originated, general conditions for thermodynamic equilibrium were established, and the theory of phases and capillarity was developed.

In the twentieth century thermodynamics developed considerably beyond the initial requirements of heat engineering and is concerned, as has already been said, with the laws of the thermal form of motion of matter mainly in equilibrium systems and in the passage of systems to an equilibrium state.

Thermodynamics is a deductive science that derives its main contents from two fundamental laws—the laws of thermodynamics, and makes use at the same time of a whole series of other experimental facts. The first law of thermodynamics expresses the quantitative aspect of the law of conservation and transformation of energy.

Although the law of conservation and transformation of energy (just as the concept itself of energy as a measure of motion) is only applicable to physical forms of motion (see § 4) and is not applicable to higher forms of motion of matter (biological and social motions), it has nonetheless a universal value. This follows from the universality of physical forms of motion: each higher form of motion of matter contains in itself physical forms of motion though it does not reduce [simply] to them. And if in the transformation of a physical form of motion into another, one of them disappears (partially or completely) while the second one increases quantitatively (the transformation of mechanical motion into thermal or electromagnetic motion and vice versa), then in the arising of a new higher form of motion of matter the various physical forms of motion generating it do not disappear but exist as "their higher unity" (see F. Engels, *The Dialectics of Nature*, page 199, 1952). The destruction of this unity leads to the vanishing of this higher form of motion and to the liberation and separation of the different physical forms of motion generating it and having their measure of energy.

Hence it follows that the law of conservation and transformation of energy is directly applicable to only physical forms of motion of matter and establishes the indestructibility and inter-transformability of only these forms of material motion, but at the same time it also

expresses the fact that motion cannot be destroyed or created in general and therefore it is indissolubly bound with the dialectic-materialistic ideology which recognizes the priority of matter with its imperishable attributes.†

From the viewpoint of this unitary scientific ideology we can categorically deny the possibility of existence of phenomena (either at the scale of our planet or at a cosmical scale) in which the law of conservation and transformation of energy be invalidated. To admit the possibility of existence of such phenomena would mean not to see in the law of conservation and transformation of energy anything more important than in any other law (for example in Boyle-Mariotte law, known from the course of general physics, $pV = \text{const}$, which can also be expressed as a law of conservation of a sum of quantities, $\log p + \log V = \text{const}$, and which is verified in processes in a rarefied gas but is not valid in a denser gas).

The second law of thermodynamics is the law of entropy. A consequence of this law is, for example, the impossibility of processes the only result of which would be the transformation of heat into work, or the spontaneous passage of heat from a *cold* body to a *hot* one when these bodies come into contact etc.

Just as the first law of thermodynamics, the second law has about ten different formulations. The majority of them are equivalent to each other and express the entire content of the law itself. However, the variety of formulations of the second principle is connected with the fact that these laws become apparent in some or other concrete phenomena, so that each of these formulations corresponds to a determinate more or less general phenomenon. The formulation that expresses the law of a phenomenon closer to our experience and practice can be taken as the initial one in establishing and analysing each of the laws.

On the basis of the first and second laws, thermodynamics investigates the properties of real systems.

Thermodynamics is applicable only to systems consisting of a large number of particles. This establishes a lower bound for the dimensions of systems to which thermodynamics is applicable. But the applicability of thermodynamics has also an upper bound: it is in-

† “Modern natural science has been compelled to borrow from philosophy the thesis of the indestructibility of motion; without this thesis natural science could no longer exist now” (F. Engels, *The Dialectics of Nature*, page 16, 1952).

applicable to systems of infinite dimensions such as the universe or an infinite part of it. The initial propositions of thermodynamics are established for finite systems but with a large number of particles and for finite intervals of time.

In 1906 to the two laws of thermodynamics there was added one more experimental fact which is referred to as Nernst's theorem. According to this theorem, at temperatures tending to the absolute zero equilibrium processes occur without entropy variation, while the entropy itself of any body tends to zero as the absolute zero is steadily approached. This theorem is of great importance for finding the entropy constants and chemical constants of substances taking part in chemical transformations.

Nernst's theorem does not follow from the first and second laws of thermodynamics but expresses a new law of nature and therefore it is often referred to as the third law of thermodynamics. It can be established by proceeding from the basic propositions of quantum statistical mechanics. Otherwise, as far as its value for thermodynamics is concerned, Nernst's theorem is less important than the first and second laws.

A great contribution to the development of thermodynamics has been given by our scientists. At the end of the nineteenth century a professor of Kiev University, N. N. Shiller, gave a new formulation of the second law of thermodynamics which in 1909 was developed by the German mathematician Carathéodory. In 1928 T. A. Afanas'yeva-Ehrenfest, by analysing critically the work of Shiller and Carathéodory, showed for the first time that the second law of thermodynamics consists of two independent propositions that are generalizations of experimental data and concern, on the one hand, states of equilibrium and, on the other hand, different processes.

Of special importance has been the role of Russian scientists in the study of critical phenomena. The concept itself of critical temperature first occurs in D. I. Mendeleyev's work. Mendeleyev established that in approaching a certain temperature, surface tension tends to zero, so that the distinction between liquid and vapour disappears. Mendeleyev called this temperature the absolute boiling point. A. G. Stoletov, M. P. Avenarius and others devoted further study to critical phenomena. The Russian scientists V. A. Mikhel'son and B. B. Golytsin gave a considerable contribution to the thermodynamics of radiation. Golytsin first introduced the concept of radiation temperature which was accepted by scientists and has been

retained to the present day. D. P. Kononov, N. S. Kurnakov and others have studied the application of thermodynamics to physical chemistry.

A great contribution to thermodynamics and statistical investigations are the works of L. D. Landau on the theory of phase transitions, the works of M. A. Leontovich on the thermodynamical functions of non-equilibrium states, N. N. Bogolyubov's works on the theory of superfluidity and superconductivity, on kinetic equations and the theory of real gases, V. K. Semenchenko's works on the theory of solutions and critical phenomena and others.

This course of thermodynamics has been organised according to the following plan: at first the initial propositions of thermodynamics are established and discussed, and the contents and main corollaries of the first and second laws are expounded, then the methods of thermodynamics are considered, and next by means of these methods the most important problems of the behaviour of systems in a state of equilibrium and in various processes are investigated.

The last chapter is devoted to the fundamentals of the theory of irreversible processes.

CHAPTER 1

BASIC CONCEPTS AND INITIAL PROPOSITIONS OF THERMODYNAMICS

THERMODYNAMICS deals with the study of the laws of thermal motion in equilibrium systems and in the transition of systems to equilibrium [states] and it also extends these laws to non-equilibrium systems.†

Before we pass to the study of properties of systems we shall firstly elucidate the content of the basic thermodynamic concepts (thermodynamic system, thermodynamic equilibrium, process, heat, work etc.) and shall discuss the initial propositions of thermodynamics. This will enable us to assess the significance and limits of applicability of thermodynamics.

§ 1. Thermodynamic system and thermodynamic parameters.

Thermodynamic equilibrium from the molecular viewpoint

Any material object, any physical body, consisting of a large number of particles is called a macroscopic system. The dimensions of macroscopic systems are always considerably larger than the dimensions of atoms and molecules.

All macroscopic attributes characterizing a system and its relation to the surrounding bodies are called macroscopic parameters. They comprise, for example, such quantities as density, volume, elasticity, concentration, polarization, magnetization etc. Macroscopic parameters are sub-divided into external and internal ones.

Quantities that are determined by the position of external bodies not entering into our system are called *the external parameters* a_i ($i = 1, 2, \dots$); for example, the volume of a system is one of its external parameters in that it is determined by the position of external bodies; the intensity of a field of force is also an external parameter since it depends on the position of the sources of the field, charges and currents, which are no part of our system, etc.

† The latter refers to the thermodynamics of irreversible processes (see Chap. II).

External parameters are, therefore, functions of the coordinates of external bodies.

Other quantities, however, that are determined by the combined motion and distribution in space of particles that are part of our system are called *internal parameters* b_j ($j = 1, 2, \dots$); for example, density, pressure, energy, polarization, magnetization etc. are internal parameters, since their value depends on the motion and position of particles of the system and of charges occurring in them.

Since the relative position in space of particles entering into our system, atoms and molecules, depends itself on the relative position of external bodies, it follows that internal parameters are determined by the position and motion of these particles and by the value of external parameters.

The set of the independent macroscopic parameters of a system determines *the state of the system*. Quantities that are independent of the previous history of the system and are fully determined by its state at a given instant (i.e. by the set of the independent parameters) are called *parameters of state*.

A state is called stationary, if the system parameters are constant with time.

If, in addition, not only are all parameters in the system constant with time, but there are no stationary currents whatsoever owing to the action of some external sources, then such a state of the system is called an *equilibrium state* (a state of *thermodynamic equilibrium*).

Thermodynamics studies mainly the properties of physical systems that are found in an equilibrium state. Usually, therefore, not all macroscopic systems but only those of them that are found in thermodynamic equilibrium are called thermodynamic systems. By analogy we call *thermodynamic parameters* those parameters that characterize a system in its thermodynamic equilibrium.

What do thermodynamic internal equilibrium parameters represent from the molecular viewpoint?

In order to clarify this, let us consider a most simple example—the density of a gas (the number of particles per unit volume of gas). If the gas is found in a non-equilibrium state the gas density will be different at different points. After some time has elapsed the gas will reach an equilibrium state† and the density $\rho = mn$ (m is the mass of a molecule and n is the number of molecules per cm^3) will have a cer-

† See § 2 on this point.

tain, macroscopically constant, equilibrium value (Fig. 1). This equilibrium value of the density ϱ_0 can be defined as the mean value of the density, $\tilde{\varrho}$, over a large interval of time T :

$$\varrho_0 = \tilde{\varrho} = \lim_{T \rightarrow \infty} \frac{1}{T} \int_0^T \varrho(t) dt. \quad (1.A)$$

Similarly, the equilibrium value of any other internal parameter is the mean value, over a long interval of time, of the function of coordinates and rates of change corresponding to this parameter.

Statistical physics, proceeding from a determinate molecular model of the structure of matter, enables us to evaluate equilibrium values of internal parameters. However, even without carrying out these calculations, we can bring to light laws of systems in equilibrium states, by

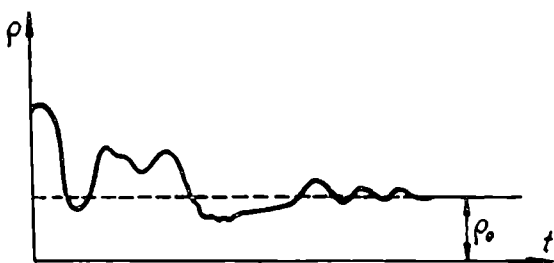


FIG. 1.

bearing in mind that in practice equilibrium parameters can be measured in many cases directly from experiment. Thermodynamics provides just this first stage in the theory of equilibrium states.

As we shall see below, systems are characterized in a state of thermodynamic equilibrium both by determined equilibrium values of the macroscopic parameters indicated above (density, pressure, volume, magnetization, etc.) and by such typically thermodynamic parameters, that in the absence of equilibrium in the system are deprived of meaning for all systems, as, for example, temperature, entropy, etc.

Thermodynamic parameters that are independent of mass or of the number of particles in the system are called *intensive parameters* (for example, pressure, temperature etc.), while those parameters that are proportional to mass and to the number of particles in the system are called additive or *extensive parameters* (for example, volume, energy, entropy, etc.).

Determined notions, based on macroscopic experiment, on the properties of the thermodynamic equilibrium of finite systems are assumed in thermodynamics as postulates, on which basis and by means of the basic laws (principles) of thermodynamics the properties of systems in equilibrium states are studied.

§ 2. Initial propositions of thermodynamics and their discussion

A system that does not exchange energy with external bodies is said to be *isolated*. External actions, by influencing the motion of particles of the system, also alter the thermal motion in it.

It is postulated in thermodynamics that, *an isolated system always reaches, in the course of time, a state of thermodynamic equilibrium and can never depart from it spontaneously (the first postulate of thermodynamics)*.

This first initial proposition of thermodynamics can be called the general principle of thermodynamics, since, similarly to the first and second laws, which establish the existence of determined functions of state, it leads to the existence of a whole series of functions of state of a system in thermodynamic equilibrium.

From the viewpoint of statistical physics, which takes into account explicitly the motion of particles in a system, the meaning of the thesis on thermodynamic equilibrium (the first postulate of thermodynamics) consists in that in each isolated macroscopic system there exists a determined and unique state that is generated by the continuously moving particles most often of all (the most probable state); an isolated system reaches in the course of time just this most probable state. It can be seen from this that the postulate of the spontaneous passing of an isolated system to equilibrium and of its remaining there for an indefinitely long time is not an absolute law of nature but merely expresses the most probable behaviour of a system; the never ceasing motion of particles of the system leads to spontaneous deviations (fluctuations) from the equilibrium state.

Thus thermodynamics, by assuming the first postulate, restricts itself, in that it renounces the consideration of all phenomena connected with the spontaneous departure of a system from its equilibrium state.

A justification for accepting the general principle of thermodynamics is the fact that, as statistical physics shows, relative spontaneous deviations of a system from equilibrium are the smaller the more particles there are in the system, and, since thermodynamic systems consist of an enormous number of particles ($N \gg 1$), fluctuations are altogether neglected in thermodynamics.

However, in those phenomena where fluctuations are essential, the thermodynamic approach to the study of these phenomena is no longer correct owing to the initial proposition assumed, and a statistical consideration is necessary. In these cases the conclusions of thermodyna-

mics and statistical physics will be at variance, which is caused by the restricted scope and relativity of the first initial proposition of thermodynamics. The clarification of this fact shows that thermodynamic and statistical considerations do not exclude, but are complementary to, each other.

The first postulate on thermodynamic equilibrium restricts, on the other hand, the application of thermodynamics when applied to infinite systems (the universe or an infinite part of it), since in a system of an infinite number of particles ($N \rightarrow \infty$) all states are equiprobable, and therefore there exists no equilibrium state (as the most probable state) to which the system should pass in the course of time.†

The second initial proposition of thermodynamics is connected with other properties of thermodynamic equilibrium as a special form of thermal motion. Experiment shows that if two equilibrium systems A and B are brought into thermal contact,‡ then, independently of whether the external parameters in them are different or equal, they either remain as before in a state of thermodynamic equilibrium, or the equilibrium in them is destroyed and, after a certain time, as a result of thermal exchange (exchange of energy) both systems reach another equilibrium state. If then this complex system is brought into thermal contact with a third equilibrium system C , then, similarly as before, either equilibrium in the systems is not altered, or is destroyed and, after a certain time, they all reach a certain new equilibrium state. If, later, thermal contact between the systems is interrupted (either simultaneously or in sequence), then, both after this and after renewed establishing of thermal contact, equilibrium in each of the systems is not altered, and therefore equilibrium of the system C separately with the systems A and B involves equilibrium of the systems A and B with one another (the transitivity property of thermodynamic equilibrium).

It follows from all this that a state of thermodynamic equilibrium of a system is determined not only by its external parameters a_i but also by another quantity t characterizing its internal state. In the presence of thermal contact of various equilibrium systems, as a result of exchange of energy, the values of this quantity t are equalized and

† See § 20 and problem no. 64.

‡ It is said of bodies that they are found in thermal contact (or else are brought into thermal contact) if, by some method or other (thermal conductivity and by means of radiation) thermal exchange is made possible for them, without it being possible for a substance that is part of one body to penetrate inside the other.

remain the same for all of them both while thermal contact lasts and after it has been discontinued.†

The transitivity property of states of thermodynamic equilibrium enables us to compare the values of the quantity t in different systems without bringing them into direct thermal contact with each other, but by making use of some other body. This quantity, expressing the state of internal motion of an equilibrium system, having one and the same value in all parts of a complex equilibrium system independently of the number of particles in them, and being determined by external parameters and by the energy corresponding to each part, is called *temperature*. Being an intensive parameter, temperature is in this sense a measure of the intensity of thermal motion.

The proposition outlined stating the existence of temperature as a special function of the state of equilibrium of a system represents the second initial proposition of thermodynamics. It is referred to sometimes as the “zero-th principle”, since, similarly to the first and second laws which establish the existence of certain functions of state, it establishes the existence of temperature in an equilibrium system.

Temperature, as we see, is a parameter of thermodynamic equilibrium since it only exists in systems in thermodynamic equilibrium, and moreover only in such systems the (macroscopic) parts of which do not interact with each other, so that the energy of the system is equal to the sum of the energies of its parts.‡

For a system close to equilibrium temperature can only be assumed as an approximate concept, and, for a system not in equilibrium, the concept of temperature is deprived of meaning altogether.

The proposition stating the existence of temperature can also be formulated in the following manner. We have established in § 1 that the internal parameters of a system are determined by the position and motion of the molecules that are part of the system and by the values of external parameters, in which connexion, to characterize a state (an equilibrium state) of the system, thermodynamics uses not actual functions of the coordinates and momentum of molecules but mean values of functions over a sufficiently large interval of time. However, the proposition on the existence of temperature establishes that

† In this connection the energy of different systems is, generally speaking, different. This follows from the identity of the separate binary equilibrium of systems $A + B$, $A + C$ and $B + C$ and of their ternary equilibrium state $(A + B) + C$.

‡ This follows from the fact that in interrupting or establishing thermal contact between parts of a system, their states, as we have observed, do not vary.

a state of thermodynamic equilibrium is determined by the set of external parameters and temperature.†

Therefore, though internal parameters characterize the state of a system, they are not independent parameters of an equilibrium system. *All equilibrium internal parameters of a system are functions of the external parameters and temperature (the second postulate of thermodynamics).*

Since the energy of a system is one of its internal parameters, then, in equilibrium, energy will be a function of external parameters and temperature. By expressing, from this equation, temperature in terms of energy and external parameters, we can formulate the second initial proposition of thermodynamics also in the following manner: under equilibrium conditions all internal parameters are functions of external parameters and energy.‡

The second initial proposition of thermodynamics enables us to determine the temperature variation of a body from the variation of any of its internal parameters, on which fact is based the construction of the various thermometers.††

In order to establish which of two temperatures is the larger, an additional condition is introduced: it is assumed that in communicating energy to a body under constant external parameters its temperature increases (although we could assume that it decreases) or else (which is found in accordance with the condition given but is not the

† Since the state of a thermodynamic system is determined by external parameters and temperature while the concept of temperature (as a measure of the intensity of thermal motion) is extraneous to mechanics, then, consequently, mechanical systems are not thermodynamic systems (they can be considered formally as a particular case of thermodynamic systems in which the intensity of thermal motion is equal to zero). It is understandable, therefore, that certain conclusions of thermodynamics are inapplicable to mechanical systems. These are mainly those results that are connected with distinctive features of thermal motion in molecular macroscopic systems (irreversibility, uniqueness of direction of natural processes etc.). Thus, to avoid misunderstandings in the definition of some or other thermodynamic concepts, it is necessary from the very beginning not to consider mechanical systems on a par with thermodynamic ones and to apply the results of thermodynamics to mechanical systems each time after special consideration, since the passage from mechanical systems to thermodynamic (statistical) ones is connected with a qualitative saltus from one form of motion to another.

‡ Equilibrium systems in which the internal parameters are functions of the external parameters and the energy are called *ergodic*. Therefore thermodynamics studies ergodic systems.

†† The fact that in thermometers, the temperature t is often determined from the volume V which is not an internal but an external parameter is explained by the existence of the equation of state (see § 5).

same†) if in the presence of thermal contact of the bodies A and B energy passes from A to B it is assumed that the temperature of the body A is larger than the temperature of the body B (though we could also have assumed the contrary). Such an additional condition to specify further the concept of temperature enables us to choose for the internal energy of a system a monotonically increasing function of temperature, which is perfectly possible as a consequence of two experimental facts: the uniqueness of the distribution of energy over the parts of the system and the simultaneous growth of the energy of parts when the total energy of the system increases (see problem 1).

In the practical determination of temperature we have to use some determined scale connected with some substance or other. As the thermometric parameter we use most often of all the volume of this substance, and the scale chosen is Celsius' scale: the difference of the volumes of the body when it is in thermal equilibrium with boiling water at atmospheric pressure and with melting ice at the same pressure is divided in 100 parts; each division corresponds to one degree and the temperature of melting ice is taken equal to 0°C .‡

We call the empirical temperature of a body a measure, determined by experiment, of the deviation of the thermodynamic state of a body from the state of thermal equilibrium with melting ice found under the pressure of one physical atmosphere.

The readings of two thermometers with different thermometric substances are never, generally speaking, coincident except at zero and 100°C , since such a determination of temperature as an objective measure of the intensity of thermal motion is arbitrary. This arbitrariness is partly removed if we use as the thermometric substance sufficiently rarefied (ideal) gases. Their coefficient of thermal expansion α does not depend either on temperature or on the nature of the gas. The scale of a gas thermometer is graduated in the same manner as the Celsius scale but the zero temperature is taken equal to $-\alpha^{-1}$ degrees Celsius (Kelvin's scale).

We shall denote temperature measured by means of an ideal gas

† Concerning this see in §§ 19 and 30.

‡ Thermometers were invented a few years after 1600 by Galileo and, independently of him, by the Dutchman Drebbel. The freezing point of water was introduced as a constant point of the thermometer in 1664 by Hooke and the boiling point in 1665 by Huygens. Celsius in 1740 began denoting the melting point of ice by 100° and the boiling point of water by 0° . Thus he introduced the centigrade scale, but the direction of this scale was opposite to the one used today.

according to Kelvin's scale by the letter T ; it is evident that $T = \alpha^{-1} + t$ where t is the temperature according to Celsius' scale. The readings of all other thermometers are reduced to the gas thermometer.

As will be shown in the sequel, the second law of thermodynamics removes all arbitrariness in the definition of temperature by enabling us to establish an absolute scale of temperature (absolute temperature) independently of both the substance chosen and any thermometric parameter whatsoever.

§ 3. Quasi-static and non-static processes

Until now we have considered the properties of systems in a state of thermodynamic equilibrium when no parameter of the system varies with time, and inside the system there are no macroscopic motions.

If some parameters of a system vary with time then we shall say that a process takes place in such system; for example, in a variation of volume a process of compression or expansion of the system takes place; in a variation of external field a process of magnetization or polarization of the system occurs, etc. If the system is moved away from a state of equilibrium and is left to itself, then, after a certain time, it will return to the initial equilibrium state. This process of transition of a system back to an equilibrium state is called *relaxation*, and the interval of time during which the system returns to a state of equilibrium is called the *relaxation time* τ .†

A process is called an *equilibrium* or *quasi-static process* if all parameters of the system vary physically indefinitely slowly, so that the system is found all the time in equilibrium states.‡ Physically an in-

† The relaxation time is different for different processes: it varies from 10^{-18} sec for the establishing of the equilibrium pressure in a gas up to several years for the equalizing of concentration in hard alloys. In thermodynamics the largest relaxation time, during which equilibrium is reached for all parameters of a given systems, is taken as the relaxation time of the system.

‡ The indication that in quasi-static processes all parameters (both intensive and extensive ones) vary physically indefinitely slowly eliminates the need for introducing the concept, unnecessary for the thermodynamic investigations, of the so-called pseudo-equilibrium processes (in which certain intensive parameters are varied artificially by a finite amount). Moreover, as can be seen from the definition given, quasi-static processes are not only indefinitely slow physically but also always begin from some equilibrium state. This removes, as unnecessary in thermodynamics, the need to underline that, although each equilibrium process is quasi-static, not every quasi-static process (defining it merely as indefinitely slow) is an equilibrium process (as an example of such non-equilibrium but indefinitely slow process, one usually cites the

definitely slow or quasi-static variation of some parameter a is called such a variation of this parameter with time that the rate of change da/dt be considerably smaller than its mean rate of variation in relaxation; thus, if the parameter a has varied by the amount Δa while the relaxation time is τ , then in quasi-static processes we have

$$\frac{da}{dt} \ll \frac{\Delta a}{\tau}. \quad (1.1)$$

If a variation of some parameter a occurs during a time t smaller than or equal to the relaxation time τ ($t \leq \tau$) so that

$$\frac{da}{dt} \geq \frac{\Delta a}{\tau}, \quad (1.2)$$

then such a process is called *non-static*.

The concept of an equilibrium process and all considerations connected with it prove possible only on the basis of the general principle of thermodynamics that an equilibrium state is not destroyed spontaneously. In fact, the direction of an equilibrium process will be fully determined by the character of the external actions if and only if spontaneous variations of the thermodynamic state of a system are excluded.

The study of equilibrium or quasi-static processes is important since it is found (this will be verified later) that in these processes a whole series of practically important quantities (work, efficiency of machines, etc.) has limit, maximum possible, values. Therefore, results obtained in thermodynamics for quasi-static processes have in thermodynamics the role of some kind of limit theorems.

§ 4. The internal energy of a system. Work and heat

Physics studies the laws of various forms of motion of matter (mechanical motion, thermal motion, electromagnetic processes, atomic and nuclear processes and the motion of micro-particles). The common measure of material motion in its transformations from one type to another is called energy. Whatever processes occur in the world,

process of thermal exchange between bodies at different temperatures, made arbitrarily slow by the introduction between them of a thermal resistance). The definition given in the text identifies equilibrium and quasi-static processes. A slowed-down thermal exchange is not an equilibrium process and therefore is non-static (though indefinitely slow) since at the initial instant, in establishing thermal contact between the bodies, equilibrium has been destroyed.

whatever conversions of forms of motion are accomplished, the total quantity of energy always remains unaltered.

The law of conservation and transformation of energy has a most important role in all natural sciences, in particular in thermodynamics, since it concerns an attribute, an inalienable property, of matter. Engels called it the "great fundamental law of motion,"† and considered the law itself the foundation stone of the principal theses of materialism.

The law of conservation and transformation of energy has both a quantitative and a qualitative aspect. The quantitative aspect of the law of conservation and transformation of energy consists in the statement that the energy of a system is a single-valued function of its state and is preserved in all processes in an isolated system, being only converted from one type to another according to a rigorously determined quantitative equivalence relationship; the qualitative side of this law consists in the never-exhausted possibility of material motion to newer and newer transformations.

Thermodynamics studies the laws of thermal motion.

Every thermodynamic system consists of a huge number of particles. The energy of these continuously moving and interacting particles is called the *energy of the system*.

The total energy of the system divides into internal and external energy. *External energy* comprises the energy of motion of the system as a whole and the potential energy of the system in a field of forces. All the remaining part of the energy of a system is called its *internal energy*.

The motion of a system as a whole and the variation of its potential energy in such a motion is not considered in thermodynamics, and therefore in thermodynamics the energy of a system is its internal energy.‡ The internal energy of a system comprises the energy of all forms of motion and interaction of the particles that are part of the system: the energy of the translational and rotational movements of the molecules and of the oscillatory motion of atoms, the energy of molecular interaction, the inter-atomic energy of filled electron levels, the inter-nuclear energy etc.

† F. Engels, *Anti-Dühring*, p. 13 (1957).

‡ The positional energy of a system in a field of external forces is part of its external energy on condition that the thermodynamic state of the system be not varied for a displacement in the field of forces. If, however, the thermodynamic state of a system is varied in its displacement in a field of forces, then a determined fraction of the potential energy forms now a part of the internal energy of the system.

The internal energy U is an internal parameter and therefore, in equilibrium, it will depend on the external parameters a_i and the temperature T

$$U = U(a_1, a_2, \dots, a_n, T). \quad (1.B)$$

The dependence of the internal energy U on the temperature T of nearly all systems encountered in the nature surrounding us is such that an unbounded increase of temperature is accompanied with an unbounded increase of the internal energy. This occurs since each molecule or any other element of an "ordinary" thermodynamic system can have an arbitrarily large value of energy.

It has been established a few years ago that there also exist systems in which, as temperature increases, the internal energy tends asymptotically to a finite limit value, since each element of the system is limited in its maximum possible energy. Such "extraordinary" systems are the sets of nuclear spins of certain crystals, i.e. the sets of nuclear magnetic moments bound at nodes of the lattice and interacting with each other when their energy of interaction with the lattice is extremely small† in comparison with the energy of spin-to-spin interactions.

In the interaction of a thermodynamic system with the surrounding medium, energy is exchanged. In this connexion two different methods of transmission of energy from the system to external bodies are possible: with variation of the external parameters of the system and without a variation of these parameters.

The first method of transmission of energy, the one connected with variation of the external parameters, is called *work*, the second method, the one without variation of the external parameters, is called *heat*, while the transmission process itself is called *thermal exchange*.

The quantity of energy transmitted by a system with variation of its external parameters, is called *work* W (and not quantity of work), while the quantity of energy transmitted by the system without variation of its external parameters is called *quantity of heat* Q . As can be seen from the definition of heat and work, these two different methods of transmission of energy considered in thermodynamics are not equivalent. In fact, whereas expended work can directly pass into an increase of any form of energy (electric, magnetic, elastic, potential energy of gravitational force etc.), heat can only pass directly (i.e. without being preliminarily converted into work) into an increase of

† On certain paradoxical properties of such systems see § 46.

the internal energy of a system. This leads to the fact that, in the transformation of work into heat, it is possible to restrict ourselves to two bodies only, the first of which (for a variation of its external parameters) transmits by thermal contact energy to the other body (without a variation of its external parameters); on the contrary in the transformation of heat into work there must be at least three bodies: a first one that gives up energy in the form of heat (thermal source), a second one that receives energy in the form of heat and yields energy in the form of work (it is called the working body), and a third one that receives energy in the form of work from the working body.

If a system does not exchange energy with surrounding bodies it is called, as has already been said, an *isolated* or *closed* system; if, however, it does not exchange energy with other bodies in the form of heat only, it is called an *adiabatically isolated* or *adiabatic* system.

The work W and the quantity of heat Q have the dimension of energy but work and heat are not forms of energy: they represent the two different methods of transmission of energy considered in thermodynamics and therefore characterize a process. The work W and the quantity of heat Q are only different from zero in a process undergone by the system; to a state of the system, however, there corresponds no value of W or Q whatsoever.

It is assumed to consider the work W as positive if it is accomplished by a system on external bodies, while the quantity of heat Q is assumed positive if energy is transmitted to the system without variation of its external parameters.†

For an indefinitely small equilibrium variation of the parameter a the work accomplished by the system is equal to

$$\delta W = A da, \quad (1.3)$$

where A is a generalized force associated with the external parameter a and which, under equilibrium conditions, is a function of the external parameters a_i and the temperature T .

For a non-static indefinitely small variation of the parameter a the work δW_n accomplished by the system is also equal to

$$\delta W_{n-st} = A_{n-st} da_{n-st}, \quad (1.4)$$

† As follows from what has been said, Q and W occurring in the equations of thermodynamics do not denote a manner of transmission but a quantity of energy obtained by a system in a corresponding manner; often, however, they are not called "quantity of heat" and "quantity of work" but simply "heat" and "work", and one speaks of the passage of "heat" into "work" and vice versa.

but, in this case, the generalized force A_n , owing to the initial propositions of thermodynamics, is not a function of a_i and T but a function of the external parameters a_i , of the internal parameters b_i and of the derivatives with respect to time of the ones and the others.

For a variation of n external parameters the work of the system is equal to

$$\delta W = \sum_i A_i da_i. \quad (1.5)$$

As follows from the definition of work and as can be seen from (1.5), in the expression of the elementary work there does not occur the differential of temperature (i.e. the coefficient of dT is equal to zero). This leads to the fact that the differential expression δW is not an exact differential (see problem no. 2). For this reason we have denoted the elementary work by δW and not by dW .

Let us give examples of expressions of elementary work accomplished by a system in certain cases:

(a) In the quasi-static expansion of a system subject to the action of all-round uniform pressure, the elementary work is equal to

$$\delta W = p dV \quad (A = p, \quad a = V), \quad (1.6)$$

where p is the pressure of a gas or liquid and dV is the volume increase connected with a displacement of external bodies; therefore in the expansion in vacuum, when external bodies are not displaced, work is equal to zero.

(b) The work of the forces of surface tension for a surface variation by $d\Sigma$ is equal to

$$\delta W = -\sigma d\Sigma \quad (a = \Sigma, \quad A = -\sigma), \quad (1.7)$$

where σ is the surface-tension coefficient.

(c) The polarization of a dielectric in an electric field is connected with a determined work. Depending on the nature of the problem considered (which determines the choice of different independent variables characterizing the state of the dielectric in the electric field) this work is different and different expressions for the work are to be used for its evaluation (see § 25 for more details).

The elementary work for a variation in the dielectric of the electric field E as a consequence of motion of the charges generating it is equal to

$$\delta W = -\frac{1}{4\pi} (E, dD) = -\frac{1}{4\pi} (E_x dD_x + E_y dD_y + E_z dD_z) \quad (1.8)$$

(the independent variable in this problem is the induction D), so that

$$\left. \begin{aligned} a_1 &= D_x, & a_2 &= D_y, & a_3 &= D_z, \\ A_1 &= -\frac{1}{4\pi} E_x, & A_2 &= -\frac{1}{4\pi} E_y, & A_3 &= -\frac{1}{4\pi} E_z. \end{aligned} \right\} \quad (1.C)$$

In the case of an isotropic dielectric when D is parallel to E this work will be

$$\delta W = -\frac{1}{4\pi} E dD \quad \left(a = D, \quad A = -\frac{1}{4\pi} E \right). \quad (1.D)$$

The polarization work proper (or polarization work in the true sense) δW_p is the work δW less the work $-d(E^2/8\pi)$ of excitation of the field in a vacuum

$$\delta W_p = \delta W + d\left(\frac{E^2}{8\pi}\right) = -E dP \quad (a = P, \quad A = -E). \quad (1.9)$$

(d) In a similar manner the elementary work for a variation in a magnet with induction B of a magnetic field H is equal to

$$\delta W = -\frac{1}{4\pi} (H, dB) = -\frac{1}{4\pi} (H_x dB_x + H_y dB_y + H_z dB_z), \quad (1.10)$$

$$(a_1 = B_x, \quad a_2 = B_y, \quad a_3 = B_z,$$

$$A_1 = -\frac{1}{4\pi} H_x, \quad A_2 = -\frac{1}{4\pi} H_y, \quad A_3 = -\frac{1}{4\pi} H_z).$$

In the case of an isotropic magnet this work will be

$$\delta W = -\frac{1}{4\pi} H dB \quad \left(a = B, \quad A = -\frac{1}{4\pi} H \right).$$

The magnetization work proper is

$$\delta W_p = -H dM \quad (1.11)$$

($a = M$ is the amplitude of the magnetization vector; $A = -H$).

Although a profound qualitative difference exists between the concepts of work and quantity of heat, these two concepts are closely related: they both express a quantity of energy transmitted to a system either with a variation of external parameters or without such a variation. Owing to this close relationship heat is often described as thermal work. For this same reason an elementary quantity of heat δQ received by a system in quasi-static processes can also be described,

similarly to an elementary work, as the product of a generalized force T (temperature) by a variation of a generalized coordinate S (entropy):

$$\delta Q = T dS. \quad (1.12)$$

However, a rigorous justification of this expression for an element of quantity of heat can only be provided by the second law of thermodynamics.

§ 5. Thermic and caloric equations of state

The second initial proposition of thermodynamics which states that equilibrium internal parameters are functions of external parameters and temperature leads to the existence of the thermic and caloric equations of state of a system, i.e. of equations connecting the temperature T , the external parameters a_i and any one internal equilibrium parameter b_k

$$b_k = f(a_1, a_2, \dots, a_n; T). \quad (1.E)$$

If the internal parameter b_k is the internal energy U : $b_k = U$, then the equation

$$U = U(a_1, a_2, \dots, a_n; T) \quad (1.13)$$

is called the energy equation or the caloric equation of state. It is thus called since, as we shall see below, we can, by its means, find the capacities for heat and other similar quantities which are measured in thermodynamics in calories.

If the internal parameter b_k is the generalized force A_i associated with the external parameter a_i : $b_k = A_i$, then the equations

$$A_i = A_i(a_1, a_2, \dots, a_n; T) \quad (i = 1, 2, \dots, n) \quad (1.14)$$

are called *thermic equations of state*. This name is due to the fact that by means of these equations temperature is evaluated.

The total number of the thermic and caloric equations of state of a system is determined by the number of its degrees of freedom, i.e. by the number of independent parameters characterizing the state of a system. As is shown by the second principle of thermodynamics, the caloric equation of state and each thermic equation of state are not independent of each other. They are connected by a partial differential equation, the analysis of which we shall deal with at the appropriate place below.

If all these equations of state, the caloric equation and the thermic equations, are known, then, by means of the first and second principles

of thermodynamics, all the thermodynamic properties of the system can be determined. To deduce the equations of state themselves on the basis of the principles of thermodynamics is impossible; they are either obtained from experiment or are found by the methods of statistical physics. This shows once more that thermodynamics and statistical physics are complementary to each other and to separate them completely is today impossible.

In studying the properties of equilibrium systems thermodynamics considers first of all the properties of *simple* systems. Simple systems are called those that are subject to the action of a single generalized force A and therefore are such that their relation with the surrounding bodies is characterized by only one external parameter a . In other words simple systems are systems with two degrees of freedom.

In the general case of a simple system the thermic equation will be

$$A = A(T, a). \quad (1.F)$$

If $A = p$ is the pressure and therefore $a = V$ is the volume of the system, the thermic equation of state of such a system will be

$$f(p, V, T) = 0, \quad (1.15)$$

and the caloric equation will be

$$U = U(V, T). \quad (1.16)$$

The thermic equation of state for the simplest simple system, an ideal gas, is Clapeyron's equation

$$pV = \nu RT \quad (1.17)$$

(ν is the number of moles of the gas).

The caloric equation of state of an ideal gas follows from Joule's law which states that its internal energy is independent of the volume

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad (1.18)$$

whence, as we shall see, on the basis of the first principle of thermodynamics

$$U = \int C_V dT \quad (1.19)$$

and, for a monatomic ideal gas for which, as experiment shows, the thermal capacity at constant volume C_V does not depend on temperature, we obtain

$$U = C_V T + U_0. \quad (1.20)$$

The equations (1.17) and (1.18) for an ideal gas are easily obtained from molecular-kinetic models (see the problem No. 9). Thus Joule's law (1.18) follows directly from the fact that for a system of non-interacting particles (an ideal gas) the internal energy is equal (in the average) to the sum of the kinetic energies of these particles, which, of course does not depend on the volume occupied by the gas at a given temperature.

For real gases more than 150 different thermic equations of state have been suggested on an empirical basis. The simplest of them and the one that correctly reproduces the qualitative behaviour of real gases even for their passage into liquid is van der Waals' equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT. \quad (1.21)$$

This equation differs from Clapeyron's equation in the presence of two correcting terms: a correction on account of the volume b of the molecules themselves and a correction on account of the so-called internal pressure a/V^2 determined by the mutual attraction of the molecules of gas (a and b are constants independent of T and p but different for different gases).

The need of introducing a correction to the volume in the equation of state of an ideal gas when this equation is applied to a real gas was first established by M. V. Lomonosov proceeding from molecular-kinetic conceptions on the nature of heat (thermal motion).

In the case of liquids, van der Waals' equation departs markedly from experimental data. In order to obtain agreement of van der Waals' equation with these data we have to use different values of a and b over different intervals of temperature and density, i.e. we have to assume them to be functions of T and p , and the dependence of a and b on T and p proves to be very complicated. The main value of van der Waals' equation consists in that it retains its meaning qualitatively, for the passage of a gas to the liquid state. From the quantitative point of view van der Waals' equation provides only a poor approximation.

More precise equations of state of a real gas are Dieterici's equations†

$$p(V - b) = RTe^{-a/RTV} \quad (1.22)$$

† See problems nos. 11 and 12.

Dieterici's first equation † and

$$\left(p + \frac{a}{V'^2}\right)(V - b) = RT \quad (1.23)$$

(Dieterici's second equation), Berthelot's equation

$$\left(p + \frac{a}{V^2T}\right)(V - b) = RT \quad (1.24)$$

and others.

Both the caloric equation and the thermic equations of state for real gases can be derived theoretically by the methods of statistical physics.

The equation of state can be written in the following standard form

$$pV = RT \left(1 + \frac{A}{V} + \frac{B}{V^2} + \frac{C}{V^3} + \dots\right), \quad (1.25)$$

where A , B , C , etc. are functions of temperature, called *virial coefficients* (respectively the first, second, third, etc. virial coefficients).

The most general equation of state of real gases, and one that expresses most completely all their thermic properties, was obtained by statistical methods by Maiyer and Bogolyubov. Maiyer-Bogolyubov's equation has the form

$$pV = RT \left[1 - \sum_{\nu, \mu} \frac{\nu}{\nu + 1} \cdot \frac{A_{\nu\mu}}{V^\nu} \cdot \frac{1}{(kT)^\mu}\right], \quad (1.26)$$

where the coefficients $A_{\nu\mu}$ are expressed in terms of the interaction potential between molecules of a given gas.

By using the thermic equation of state $f(p, V, T) = 0$ for a simple system, we can easily find the following three thermic coefficients often used in practice: the coefficient of thermal expansion

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p, \quad (1.27)$$

the coefficient of isothermal compression

$$\beta = -\frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_T, \quad (1.28)$$

the thermal coefficient of pressure (elasticity)

$$\gamma = \frac{1}{p_0} \left(\frac{\partial p}{\partial T} \right)_V. \quad (1.29)$$

† Dieterici's first equation has the form $p(V - b) = RT \exp(-\alpha/RT\gamma V)$, where γ is a number close to 1 ($\gamma = 12.7$).

These coefficients are connected with each other by the relation (see problem No. 8)

$$\alpha = p_0 \beta \gamma, \quad (1.30)$$

which is very important in practice for the determination of γ in solid and liquid bodies, since it is impossible to raise the temperature of a body, without a variation of its volume (or of the envelope in which it is contained).

PROBLEMS

1. Show that the two following experimental facts: the uniqueness of the energy distribution of an equilibrium system among its parts and the simultaneous increase of the energy of these parts for an increase of the total energy of the system, enable us to choose for the internal energy a monotonically increasing function of temperature.

2. Show that the differential expression for the elementary work

$$\delta W = \sum_i A_i da_i \quad (1.G)$$

is not an exact differential.

3. Evaluate the work of evaporation of one mole of water when this is converted into vapour at 100°C and under normal pressure. Determine also the quantity of heat communicated at the same time.

4. Evaluate the work accomplished by the unit volume of the core of a long solenoid when its magnetic polarity is reversed twice, if it is known that the area of the loop of the hysteresis curve for the core in the coordinates H and M is equal to S .

5. Show that the elementary work of polarization per unit volume of an isotropic dielectric is equal to

$$\delta W = -\frac{1}{4\pi} E dD, \quad (1.H)$$

while the elementary work of polarization proper (see p. 25) is equal to

$$\delta W_p = -E dP. \quad (1.J)$$

6. Transverse waves of frequency ν and amplitude a are propagated from left to right along a string. The tension of the string is equal to T . Determine the work accomplished per period by the portion of string situated on the left of a certain point of the string on the portion of the string situated on the right of this point.

7. Establish that for any simple system subject to the action of a generalized force A (associated with the external parameter a) the following identity is valid

$$\left(\frac{\partial T}{\partial A}\right)_a \left(\frac{\partial A}{\partial a}\right)_T \left(\frac{\partial a}{\partial T}\right)_A = -1. \quad (1.K)$$

8. Establish the connexion between the thermic coefficients α , β and γ .

9. Considering an ideal gas as a set of non-interacting continuously moving particles, find for it the thermic and cloric equations of state.

10. At a certain temperature $T = T_c$ and a certain pressure $p = p_c$ the difference between the specific volumes of liquid V_l and gas V_g vanishes ($V_l = V_g = V_c$). Such a state of a substance is called critical, while the values of the parameters T_c , p_c and V_c for which this occurs are called critical parameters.

Express the critical parameters V_c , p_c and T_c of a van der Waals' gas in terms of the constants a and b of this gas and evaluate the critical coefficient

$$s = \frac{RT_c}{p_c V_c}. \quad (1.L)$$

11. Find expressions of the critical parameters V_c , p_c and T_c by proceeding from Dieterici's equation

$$p(V-b) = RTe^{-a/RTV}. \quad (1.M)$$

Evaluate the critical coefficient $s = RT_c/p_c V_c$ for this equation and compare it with the experimental value and the value obtained from van der Waals' equation. Show that for large volumes Dieterici's equation reduces to van der Waals' equation.

12. Evaluate the critical coefficient s for Dieterici's second equation

$$\left(p + \frac{a}{V^2}\right)(V-b) = RT \quad (1.N)$$

and compare it with the experimental value and the value obtained from van der Waals' equation.

13. If the critical parameters are used as units for the measurement of pressure, volume and temperature, we obtain the reduced variables

$$\pi = \frac{p}{p_c}, \quad \varphi = \frac{V}{V_c}, \quad \tau = \frac{T}{T_c}. \quad (1.O)$$

The equation of state in these variables is called the reduced equation of state.

Obtain van der Waals' reduced equation and the reduced equation for Dieterici's first equation. Is it always possible to obtain a reduced equation of state from a given equation of state? Show that in all cases when the volume of a gas is large in comparison with its critical volume van der Waals' equation reduces to Clapeyron's equation.

14. Find the values of the first and second virial coefficients of a van der Waals' gas and the temperature value at which the first virial coefficient is equal to zero (Boyle's point).

CHAPTER II

FUNDAMENTAL LAWS AND EQUATIONS OF THERMODYNAMICS. THE FIRST LAW OF THERMODYNAMICS

THERMODYNAMICS is a deductive science. Its progress is essentially characterized by the fact that it obtains a great number of relations between quantities that determine the state of bodies on the basis of very general empirical laws, namely the laws of thermodynamics.

Thus, for example, it establishes a connection between the thermal capacities C_p and C_v , shows that $C_p > C_v$, finds a relation between these thermal capacities and the elasticity moduli, defines quantities the variations of which indicate the direction of natural processes, obtains equilibrium conditions etc. Thermodynamics cannot, however, determine the functional dependence of thermal capacity on temperature, cannot obtain the equation of state, leaves the so-called entropic and chemical constants undetermined etc. When approaching the study of phenomena from a purely thermodynamical viewpoint, all these data must be taken from experiment. Such a study cannot of course be considered definitive and complete; this raises the need for a molecular-statistical approach to the study of phenomena, which is just the content of statistical physics.

The results of thermodynamics have the advantage of being based on the most general empirical laws without being tied to any particular conception of the properties of the particles that make up a system (a system of classical particles, a system of Bose-Einstein's quantum particles, a system of Fermi-Dirac's quantum particles etc.); the relations of thermodynamics are indeed true for all statistical systems. The laws of thermodynamics, expressed quantitatively in the form of determined equations are the basic equations of thermodynamics.

We shall proceed now to discuss the contents of these basic laws and the basic equations of thermodynamics corresponding to them.

§ 6. The equation of the first law of thermodynamics

The first law of thermodynamics is a mathematical formulation of the quantitative aspect of the law of conservation and transformation of energy. It has been established as a result of experimental and theoretical investigations in the domain of physics and chemistry, the concluding stage of which was the discovery of the equivalence of heat and work, i.e. the discovery of the fact that the transformation of heat into work and of work into heat is always accomplished according to one and the same rigorously constant quantitative relation.†

The first law of thermodynamics establishes that *the internal energy of a system is a single-valued function of its state and varies only under the influence of external actions.*

Two types of external actions are considered in thermodynamics: actions connected with a variation of the external parameters of the system (the system accomplishes work), and actions not connected with variation of external parameters but causing a variation of internal parameters or temperature (a certain quantity of heat is communicated to the system).

In integral form, i.e. for a finite process, the first law is described thus

$$U_2 - U_1 = Q - W, \quad (2.A)$$

or

$$Q = U_2 - U_1 + W, \quad (2.1)$$

† The impossibility of a mechanical perpetual motor, i.e. of such a device as would enable us by its means to obtain mechanical work without the expenditure of any energy, had already been discovered in the eighteenth century. In 1748 M. L. Lomonosov in a letter to Euler, stating his thoughts on the law of conservation of matter and extending it to material motion, wrote: "a body that by its impetus stimulates another body into motion loses as much motion as it communicates to the other". In 1755 the French Academy of Sciences declared "once and for ever" that it would no longer accept any projects of perpetual motors. In 1840 H. H. Hess formulated the law of the independence of the heat effect of chemical reactions of intermediate reactions. In 1842–1850 a whole series of investigators (Mayer, Joule, Helmholtz and others) arrived at the discovery of the equivalence of heat and work, and the mechanical equivalent of heat was determined: 1 kcal = 427 kg. The establishing of the equivalence principle was the last stage in the formulation of the quantitative aspect of the law of conservation and transformation of energy, and therefore the date of the establishing of this principle is usually identified with the date of the discovery of the first law of thermodynamics.

It can be seen from the historical information above that several decades were required in order that science could move all the way from the mere conviction of the impossibility of a perpetual motor to the modern form of the law of conservation and transformation of energy.

where $U_2 - U_1$ is the variation of internal energy of the system for the transition from a first to a second state, Q is the quantity of heat received in this connection by the system and W is the work accomplished by the system. According to the first law the variation of internal

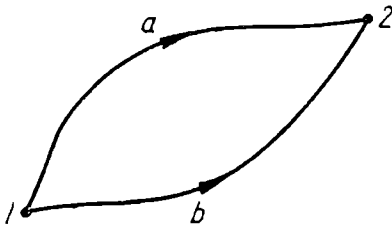


FIG. 2.

energy $U_2 - U_1$ will be one and the same independently of the path taken by the system for passing from the state 1 to the state 2 (Fig. 2), whether the path denoted conventionally by a or the path denoted conventionally by b is used; however, Q and W will be different. This means that Q and W are not functions of state but characterize a

process and, if there is no process, the system will have neither Q nor W while the internal energy always exists.

The dependence of Q and W on the path can be seen from the elementary example of the expansion of a gas. The work for the passage of the system from 1 to 2 (Fig. 3) along the path a

$$W_a = \int_{1(a)}^2 p(V, T) dV \quad (2.B)$$

is represented by the area bounded by the contour $A1a2BA$, while the work for the passage along the path b is represented by the area bounded by the contour $A1b2BA$:

$$W_b = \int_{1(b)}^2 p(V, T) dV. \quad (2.C)$$

The difference of W_a and W_b is explained by the fact that, since the pressure depends not only on the volume but also on the temperature, then in the presence of different temperature variations along the paths a and b in passing from one and the same initial state (p_1, V_1) to one and the same final state (p_2, V_2) a different work is obtained. It can be seen from this that in the closed process (cycle) $1a2b1$ the system accomplishes work that is not equal to zero. On this is based the work of all heat engines.

It follows from the first law of thermodynamics that work can be accomplished either at the expense of a variation of internal energy or at the expense of communicating to the system a quantity of heat.

In the case when the process is cyclical the initial and final stages coincide, $U_2 - U_1 = 0$ and $W = Q$, i.e. in a cyclical process, work can be accomplished only at the expense of heat received by the system from external bodies.

For this reason the first law is often formulated as a proposition stating the impossibility of a perpetual motor of the first kind, i.e. the impossibility of such periodically acting device as would accomplish work without receiving energy from without.

The proposition of the impossibility of a perpetual motor of the first kind admits of another formulation: work cannot be created from nothing or be reduced to nothing. The equation that expresses the first law for an elementary process will be

$$\delta Q = dU + \delta W, \quad (2.2)$$

or

$$\delta Q = dU + \sum_{(i)} A_i da_i. \quad (2.3)$$

In such a form the first law can describe both quasi-static and non-static processes. In these cases, however, the difference will consist in that, while in the first case the generalized forces are functions of only the external parameters a_i and the temperature T , in the second case they depend on external and internal parameters and their derivatives with respect to time.†

The work produced by a system in a non-static process is always less than the work produced in a quasi-static process

$$W_{n-st} < W_{st}. \quad (2.4)$$

This is particularly clear in the example of the expansion or compression of a gas. In the non-static expansion of a gas the external pressure p' is smaller than the initial equilibrium pressure p of the gas and therefore $p'dV < pdV$; in non-static compression, on the contrary, the external pressure p'' is larger than the equilibrium pressure and, since in this case the work is negative, we have also here

$$p'' dV < pdV. \quad (2.D)$$

† See page 14

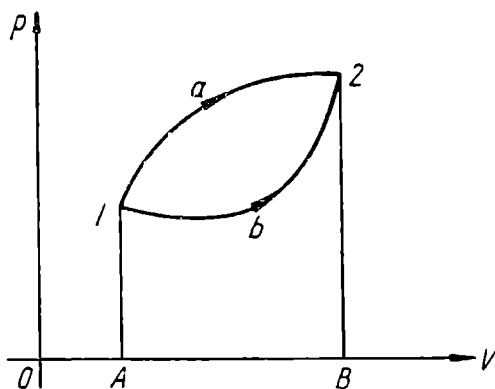


FIG. 3.

In the general case of an arbitrary non-static process we can prove this theorem of maximum work for equilibrium processes only by proceeding from the second law of thermodynamics.

In *adiabatic processes* ($\delta Q = 0$), on the basis of the first law of thermodynamics, the work for both quasi-static and non-static processes is equal to one and the same quantity, $U_2 - U_1$.

We shall now consider several consequences and applications of the first law of thermodynamics.

§ 7. Thermic and caloric properties. Thermal capacities and latent heats. Connexion between thermal capacities

The properties of systems studied in thermodynamics can be divided into thermic and caloric properties. The phenomena that are connected with a variation of external parameters a (for example, the volume V) or the generalized forces A corresponding to them (for example, the pressure p) for a variation of temperature, are called thermic properties of a substance; the phenomena, however, that are connected with a variation of only the internal energy or of the internal energy together with a variation of other internal parameters for a variation of temperature and external parameters, are called caloric properties of the system.

Accordingly, as we already know, an equation of the form

$$A = A(a, T) \quad (2.E)$$

(in the particular case, $p = p(V, T)$) is called the thermic equation of state of a simple system, while the equation

$$U = U(a, T) \quad (2.F)$$

(in the particular case, $U = U(V, T)$) is called the caloric equation of state. The set of these two equations of state enables us to determine both thermic and caloric properties.

To determine the caloric properties we need to know, generally speaking, both the thermic and the caloric equations of state. The caloric properties comprise, first of all, thermal capacities and latent heats.

The thermal capacity is defined as the quantity of heat that is needed for raising the system temperature by 1°C , i.e.

$$C = \frac{\delta Q}{dT} . \quad (2.G)$$

Since, however, the quantity of heat δQ depends on the nature of the process, then the system thermal capacity will also depend on the conditions under which the ratio $\delta Q/dT$ is determined. One and the same system exhibits many different thermal capacities, depending on the process undergone by it. Numerically the quantity C can vary within the limits $-\infty$ to $+\infty$.† Of the greatest practical value are the thermal capacities C_p and C_v .

On the basis of the first law of thermodynamics expressions can be found for these thermal capacities (in terms of the caloric and thermic equations of state), and the connection between them can be established. In fact, since we have in general for a simple system

$$\delta Q = dU + A da \quad \text{and} \quad U = U(a, T) \quad (2.H)$$

then

$$\delta Q = \left(\frac{\partial U}{\partial T} \right)_a dT + \left[\left(\frac{\partial U}{\partial a} \right)_T + A \right] da, \quad (2.J)$$

and

$$C = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_a + \left[\left(\frac{\partial U}{\partial a} \right)_T + A \right] \cdot \frac{da}{dT}, \quad (2.K)$$

whence

$$C_a = \left(\frac{\partial U}{\partial T} \right)_a, \quad (2.5)$$

$$C_A = \left(\frac{\partial U}{\partial T} \right)_a + \left[\left(\frac{\partial U}{\partial a} \right)_T + A \right] \left(\frac{\partial a}{\partial T} \right)_A \quad (2.6)$$

and

$$C_A - C_a = \left[\left(\frac{\partial U}{\partial a} \right)_T + A \right] \left(\frac{\partial a}{\partial T} \right)_A. \quad (2.7)$$

In the case $A = p$ and $a = V$ we obtain

$$C_p - C_v = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p. \quad (2.8)$$

We shall see from these expressions for the thermal capacities and their difference that to determine C_v we need to know only the caloric equation, while to determine C_p and $C_p - C_v$ we need to know both the thermic and caloric equations of state of the substance. The second law of thermodynamics, by establishing a connection between these equations of state, makes it unnecessary to know the caloric equation

† The definition of thermal capacity is closely connected with the concept of thermostat, which is widely employed in thermodynamics. In thermodynamics we call *thermostat* a body having a very large thermal capacity ($C \rightarrow \infty$), so that when this body exchanges heat with some system its temperature is not varied.

in order to determine $C_p - C_v$ (see § 17). According to the definition of the concept of "higher temperature", we assume in thermodynamics $C_v = (\partial U / \partial T)_v > 0$ (and, in general, $C_a = (\partial U / \partial T)_a > 0$).

The thermic equation of state for an ideal gas is Clapeyron's equation

$$pV = \nu RT. \quad (1.17)$$

The caloric equation of state of an ideal gas can be established by proceeding from the Gay-Lussac and Joule-Thomson experiments. According to these experiments, in the adiabatic expansion of a rarefied gas in a vacuum the temperature of such a gas does not vary. Hence *Joule's law* follows: *the energy of an ideal gas depends only on temperature and does not depend on its volume*. In fact, since in an adiabatic expansion in a vacuum $\delta Q = 0$ and $\delta W = 0$, and therefore $dU = 0$, then, since at the same time (according to Gay-Lussac's experiments) the temperature does not vary ($dT = 0$), from

$$dU = \left(\frac{\partial U}{\partial V} \right)_v dT + \left(\frac{\partial U}{\partial T} \right)_v dV = 0 \quad (2.1)$$

we obtain

$$\left(\frac{\partial U}{\partial V} \right)_T = 0. \quad (2.9)$$

It is found experimentally that the C_v of monatomic gases is independent of temperature, whereas in other ideal gases there exists a weak dependence of the thermal capacity C_v on temperature, which is not difficult to understand if one proceeds from molecular models of polyatomic ideal gases.

Considering that in ideal monatomic gases C_v is constant, we shall obtain for them the caloric equation of state:

$$U = C_v T + U_0. \quad (2.10)$$

On the basis of Clapeyron's equations and Joule's law for ideal gases we obtain

$$C_p - C_v = \nu R, \quad (2.11)$$

whence we obtain for the molecular thermal capacities ($\nu = 1$)

$$C_p - C_v = R, \quad (2.12)$$

$$R = 8.314 \times 10^7 \frac{\text{erg}}{\text{degree} \times \text{mole}} = 1.987 \frac{\text{cal}}{\text{degree} \times \text{mole}} \approx 2 \frac{\text{cal}}{\text{degree} \times \text{mole}}$$

and for the specific thermal capacities

$$c_p - c_v = \frac{R}{\mu}, \quad (2.13)$$

where μ is the molecular weight of the gas.

In the case of complex systems when

$$A_i = A_i(a_1, a_2, \dots, a_n; T) \quad \text{and} \quad U = U(a_1, a_2, \dots, a_n; T) \\ (i = 1, 2, 3, \dots, n), \quad (2.0)$$

the thermal capacity is equal to

$$C = \frac{\delta Q}{dT} = \left(\frac{\partial U}{\partial T} \right)_{a_1, a_2, \dots, a_n} + \sum_{(i)} \left[\left(\frac{\partial U}{\partial a_i} \right)_{a_1, a_2, \dots, T} + A_i \right] \frac{da_i}{dT}. \quad (2.P)$$

Thermal capacities of the form C_{a_1, \dots, a_k} , C_{a_1, \dots, A_k} , C_{A_1, \dots, A_k} etc. can be determined from this expression.

Together with thermal capacities latent heats have great importance in the thermodynamic study of properties of systems. *Latent heat* is the quantity of heat that is needed for a unit variation of an external parameter when temperature and the other external parameters remain constant:

$$l_{a_i} = \left(\frac{\delta Q}{\partial a_i} \right)_{T, a_1, \dots, a_n}. \quad (2.12)$$

For example, the latent heat of expansion is equal to

$$l_V = \left(\frac{\delta Q}{\partial V} \right)_{T, a_1, \dots, a_n}. \quad (2.Q)$$

It follows from the equation of the first law of thermodynamics

$$\delta Q = dU + \sum_{(i)} A_i da_i = \left(\frac{\partial U}{\partial T} \right)_{a_1, \dots, a_n} dT + \sum_{(i)} \left[\left(\frac{\partial U}{\partial a_i} \right) + A_i \right] da_i \quad (2.R)$$

that

$$l_V = \left(\frac{\partial U}{\partial V} \right)_{T, a_1, \dots, a_n} + p \quad (2.13)$$

and, in general, the latent heat of the variation of the external parameter a_i is equal to

$$l_{a_i} = \left(\frac{\partial U}{\partial a_i} \right)_{T, a_1, a_2, \dots, a_{i-1}, a_{i+1}, \dots, a_n} + A_i \quad (i = 1, 2, \dots, n); \quad (2.14)$$

the latent heat of expansion of an ideal gas is equal to

$$l_V = p. \quad (2.S)$$

The differential equation of the first law can now be written in the form

$$\delta Q = C_{a_1, a_2, \dots, a_n} dT + \sum_{(i)} l_{a_i} da_i. \quad (2.15)$$

Such a differential linear form in the total differentials of the independent variables T, a_1, a_2, \dots, a_n is called Pfaff's form.

§ 8. Fundamental thermodynamic processes and their equations

In every thermodynamic system (whether simple or complex) three processes are always possible: an *isothermal* process ($T = \text{const}$), an *adiabatic* process ($\delta Q = 0$) and a *polytropic* process (the thermal capacity C is constant). The number and characteristics of other possible processes depend on the nature of the system: in more complex systems a greater number of different processes is possible. In a simple system having an external parameter a and, associated with it, a force parameter A , two more processes are possible in addition to the three indicated above: a process with $a = \text{const}$ and a process with $A = \text{const}$. If the external parameter is the volume of the system ($a = V$ and, consequently, $A = p$), then the $V = \text{const}$ process is called *isochoric* and the $p = \text{const}$ process is called *isobaric*. These five processes (isothermal, adiabatic, polytropic, isochoric and isobaric) are basic in thermodynamics, the adiabatic process being, of course, a particular case of polytropic process† ($C = 0$).

The functional relation occurring among the quantities T , V and p in a certain process is called the equation of this process. The equations of the isothermal, isochoric and isobaric processes are directly obtained from the equation of state of the system, for $T = \text{const}$, $V = \text{const}$ and $p = \text{const}$ respectively

$$\begin{aligned} f_{T=\text{const}}(p, V, T) &= 0, \\ f_{V=\text{const}}(p, V, T) &= 0, \\ f_{p=\text{const}}(p, V, T) &= 0. \end{aligned} \tag{2. T}$$

In the case of so simple a system as an ideal gas, the thermic equation of state of which is Clapeyron's equation, we have:

the equation of an isothermal process: $pV = \text{const}$;

the equation of an isochoric: $p = aT$, $a = R/V = \text{const}$;

the equation of an isobaric: $V = a_1T$, $a_1 = R/p = \text{const}$.

As to the equations of adiabatic and polytropic processes, these cannot be obtained using merely the thermic equation of state; to obtain the equations of these processes the caloric equation of state is also required since neither the elemental quantity of heat δQ nor the thermal capacity C , which determine respectively the first and second of these processes, occur in the thermic equation of state.

We shall determine the equation of a polytrope and its particular

† Formally, also an isothermal process can be considered as a polytropic process ($C = \infty$).

case, the equation of an adiabatic, for an arbitrary simple system and, in particular, for an ideal gas.

In a polytropic process $\delta Q = C dT$ where $C = \text{const}$ (for an adiabatic process $C = 0$), and therefore the equation of the first law of thermodynamics for a simple system in the general case

$$\delta Q = dU + A da \quad (2. U)$$

assumes the form

$$C dT = C_a dT + \left[\left(\frac{\partial U}{\partial a} \right)_T + A \right] da. \quad (2. V)$$

By using the relation (2.7) we shall obtain

$$(C - C_a) dT = \frac{C_A - C_a}{\left(\frac{\partial a}{\partial T} \right)_A} da, \quad (2.16)$$

and, if $C \neq C_a$, then

$$dT + \frac{C_A - C_a}{C_a - C} \left(\frac{\partial T}{\partial a} \right)_A da = 0. \quad (2.17)$$

This equation is the differential equation of a polytrope in the variables T and a .

In the variables A and a the differential equation of a polytrope can be obtained if we find from the equation of state $T = T(A, a)$

$$dT = \left(\frac{\partial T}{\partial A} \right)_a dA + \left(\frac{\partial T}{\partial a} \right)_A da \quad (2.W)$$

and substitute in (2.17); then we shall obtain

$$\left(\frac{\partial T}{\partial A} \right)_a dA + \frac{C_A - C}{C_a - C} \cdot \left(\frac{\partial T}{\partial a} \right)_A da = 0. \quad (2.18)$$

Hence the differential equation of the adiabatic ($C = 0$) of a simple system has the form

$$\left(\frac{\partial T}{\partial A} \right)_a dA + \gamma \left(\frac{\partial T}{\partial a} \right)_A da = 0, \quad (2.19)$$

where

$$\gamma = \frac{C_A}{C_a}. \quad (2.X)$$

In order to integrate the equations of either a polytrope or an adiabatic we need to know both the thermic equation of state (from which $(\partial T / \partial A)_a$ and $(\partial T / \partial a)_A$ are determined) and the caloric equation of state for determining C_A and C_a .

If the system is found under the action of a force of uniform pressure when $A = p$ and $a = V$, then the equation of a polytrope† and of an adiabatic will be respectively

$$\left(\frac{\partial T}{\partial p}\right)_V dp + \frac{C_p - C}{C_V - C} \left(\frac{\partial T}{\partial V}\right)_p dV = 0 \quad (2.20)$$

and

$$\left(\frac{\partial T}{\partial p}\right)_V dp + \gamma \left(\frac{\partial T}{\partial V}\right)_p dV = 0. \quad (2.21)$$

On the basis of Joule's law (2.9), C_p and C_V in the case of an ideal gas depend only on temperature, γ being equal to 1.66 and independent of temperature for monatomic gases, while for diatomic gases γ decreases with an increase of temperature and is equal to 1.4 at room temperature.

For a monatomic ideal gas, by substituting in the differential equation of a polytrope the derivatives $(\partial Z/\partial p)_V$ and $(\partial T/\partial V)_p$ determined from Clapeyron's equation, we shall obtain, after integrating, the equation of a polytrope

$$pV^n = \text{const}, \quad (2.22)$$

where $n = (C_p - C)/(C_V - C)$ is the index of the polytrope.

The equation of the adiabatic for this gas

$$pV^\gamma = \text{const} \quad (2.23)$$

is called the equation of *Poisson's adiabatic*.

Since the thermal capacities C_V and C_p of a monatomic ideal gas are independent of temperature and are constants, then isochoric and isobaric processes for such a gas (and only for it) are also polytropic.

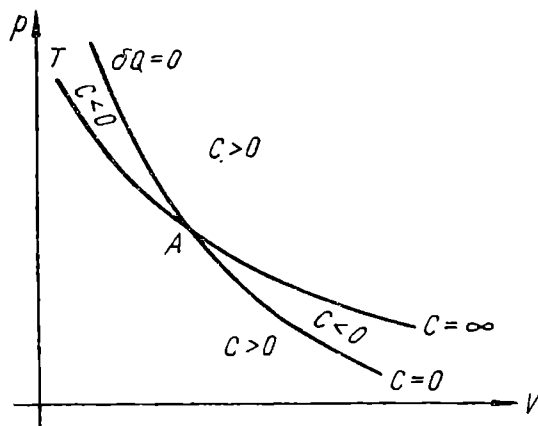


FIG. 4.

isochoric and isobaric processes for such a gas (and only for it) are also polytropic.

Quasi-static processes can be represented graphically on various diagrams with suitable coordinate axes. The diagrams most used in thermodynamics are the work diagram with the V and p axes (an element of

† It is easily verified that from the equation of a polytrope (2.20) we cannot obtain the differential equations of an isobaric and an isochoric process.

area in this diagram represents work) and the so-called entropy diagram with S and T axes (see § 18).

Through each point on the V, p diagram we can draw an isothermal and an adiabetic. The slope of these curves with respect to the axis of the abscissae is determined respectively by the derivatives $(\partial p/\partial V)_T$ and $(\partial p/\partial V)_{ad}$.

We have for an isothermal of an ideal gas $(\partial p/\partial V)_T = -p/V$ and for an adiabetic of an ideal gas $(\partial p/\partial V)_{ad} = -\gamma p/V$. Thus, since $\gamma = C_p/C_v > 1$, the slope of the adiabetic with respect to the axis of the abscissae is larger than that of the isothermal (Fig. 4). Between the curves corresponding to $C = 0$ and $C = \infty$ there are found the curves of all other polytropic processes having thermal capacities within the limits

$$-\infty < C < \infty \quad (2. Y)$$

(see problem no. 26).

§ 9. The connexion between elasticity coefficients and thermal capacities

The first law of thermodynamics enables us to establish a connection between the elasticity coefficients and thermal capacities.

The elasticity modulus of a system, ε , determines the variation of pressure for a unit relative variation of volume and is the reciprocal of volume compressibility

$$\varepsilon = - \frac{dp}{\frac{dV}{V}} = -V \frac{dp}{dV}. \quad (2. Z)$$

The minus sign is affixed to make ε positive, since, as we shall see, dp and dV for stable states have different signs. The value of the elasticity modulus depends on the value of the derivative dp/dV , i.e. it depends on the conditions under which compression takes place.

The most common ones are the isothermal elasticity modulus

$$\varepsilon_T = -V \left(\frac{\partial p}{\partial V} \right)_T \quad (2. 24)$$

and the adiabetic elasticity modulus

$$\varepsilon_S = -V \left(\frac{\partial p}{\partial V} \right)_S. \quad (2. 25)$$

The ratio of these moduli is equal to

$$\frac{\varepsilon_s}{\varepsilon_T} = - \frac{\left(\frac{\partial p}{\partial V}\right)_s}{\left(\frac{\partial p}{\partial V}\right)_T}. \quad (2. AA)$$

From the differential equation of an adiabatic we have

$$\left(\frac{\partial p}{\partial V}\right)_s = -\gamma \frac{\left(\frac{\partial T}{\partial V}\right)_p}{\left(\frac{\partial T}{\partial p}\right)_V}, \quad (2. AB)$$

while, from the equation of state $T = T(V, p)$, we have

$$dT = \left(\frac{\partial T}{\partial V}\right)_p dV + \left(\frac{\partial T}{\partial p}\right)_V dp, \quad (2. AC)$$

and for an isothermal process ($dT = 0$)

$$\left(\frac{\partial p}{\partial V}\right)_T = - \frac{\left(\frac{\partial T}{\partial V}\right)_p}{\left(\frac{\partial T}{\partial p}\right)_V}. \quad (2. AD)$$

Therefore

$$-\frac{\left(\frac{\partial p}{\partial V}\right)_s}{\left(\frac{\partial p}{\partial V}\right)_T} = \gamma \quad (2. AE)$$

and hence

$$\frac{\varepsilon_s}{\varepsilon_T} = \gamma, \quad (2. 26)$$

i.e. the ratio of the isothermal to the adiabatic elasticity modulus is equal to the ratio of the thermal capacities. In so far as $\gamma > 1$ † it follows that $\varepsilon_s > \varepsilon_T$. By measuring ε_s and ε_T experimentally we can find γ .

In the general case of a simple system when the generalized force

† See problem no. 17.

is equal to A and the external parameter associated with it is a , the ratio of the adiabatic modulus of variation of the quantity A

$$\varepsilon_S = -a_0 \left(\frac{\partial A}{\partial a} \right)_S \quad (2.27)$$

to the isothermic modulus of variation of this quantity

$$\varepsilon_T = -a_0 \left(\frac{\partial A}{\partial a} \right)_T \quad (2.28)$$

is equal to

$$\frac{\varepsilon_S}{\varepsilon_T} = \frac{C_A}{C_a}, \quad (2.29)$$

where C_A and C_a are the thermal capacities respectively for A and a constant.

§ 10. Hess's rule. Thermochemical equations

The first law of thermodynamics enables us to obtain Hess's rule which was discovered by this scientist in 1840 before the first law had been formulated. Hess's rule (or the law of constancy of heat sums) indicates that the heat released or absorbed in a chemical reaction occurring at a constant volume V , or at a constant pressure p , is independent of any intermediate reactions and is determined only by the initial and final states of the reacting substances.

This rule is a consequence of the first law of thermodynamics. In fact, if $V = \text{const}$ then, from $\delta Q = dU + p dV$ we obtain

$$Q = U_2 - U_1, \quad (2.AF)$$

i. e. the quantity of heat does not depend on the path taken to move from the first state to the second. If a reaction occurs at $p = \text{const}$ then

$$\delta Q = dU + p dV = d(U + pV), \quad (2.AG)$$

and the quantity of heat

$$Q = (U_2 + pV_2) - (U_1 + pV_1) \quad (2.AH)$$

will also be independent of the path.

Hess's rule enables us to evaluate the heat released or absorbed in such reactions as do not occur spontaneously or such that the heat released or absorbed in them cannot be measured directly. In such cases we write [a system of] thermochemical equations and by solving them we determine the heat effect of the required reaction.

Thermochemical equations are equations of a chemical reaction in which instead of the symbols of the reacting substances we write the internal energies of these substances and the heat effects of the reactions. In this connexion, since a substance in different states of aggregations (with different internal energies) is represented by one and the same symbol, the convention is used of denoting the internal energy of solid substances by using square brackets, of liquids by round brackets and of gaseous substances by curled brackets. Thus the symbols $[H_2O]$, (H_2O) and $\{H_2O\}$ denote respectively the internal energy of ice, water and water vapour.

Let us show an example of the solution of thermochemical equations for evaluating the heat effect of the reaction of incomplete combustion of solid carbon into carbon

monoxide. This heat cannot be measured directly since carbon never combines with oxygen to form only carbon monoxide but always forms also a certain amount of carbon dioxide CO_2 .

It is known that in the complete combustion of carbon 97 kcal/mole are produced, while in the combustion of carbon monoxide into carbon dioxide 68 kcal/mole of CO_2 are produced. The thermochemical equations of these reactions have the form

$$\begin{aligned} [\text{C}] + \{\text{O}_2\} - \{\text{CO}_2\} &= 97, \\ \{\text{CO}\} + \frac{1}{2}\{\text{O}_2\} - \{\text{CO}_2\} &= 68. \end{aligned} \quad (2. \text{AJ})$$

By subtracting from the first equation the second one, we shall obtain

$$[\text{C}] + \frac{1}{2}\{\text{O}_2\} - \{\text{CO}\} = 29, \quad (2. \text{AK})$$

i.e. in the incomplete combustion of carbon there are produced 29 kcal/mole of CO.

The heat effect of a reaction depends on the temperature and pressure at which the reaction occurs. Unless it be especially declared, it is usually assumed that pressure is atmospheric pressure and temperature is room temperature (18°C).

The manner of temperature dependence of the heat effect of a reaction is determined by Kirchhoff's equation, which is easily established on the basis of the first law of thermodynamics (see problem no. 25).

PROBLEMS

15. Show that the elemental quantity of heat δQ is not a total differential.
16. Show that

$$C_p - C_v = \left[V - \left(\frac{\partial H}{\partial p} \right)_T \right] \left(\frac{\partial p}{\partial T} \right)_V, \quad (2. \text{AL})$$

where $H = U + pV$.

17. One of the most accurate experimental methods for the determination of the ratio $\gamma = C_p/C_v$ is the measurement of the velocity of sound in the gas investigated. Find the connection between the velocity of sound, the ratio of the thermal capacities γ and the isothermal elasticity modulus. What is the velocity of sound equal to in an ideal gas?

18. Find the difference of the thermal capacities $C_{pH} - C_{pM}$ for an ideal paramagnet (the internal energy of such a paramagnet depends only on temperature).

19. Find the equation of the adiabatic for an ideal paramagnet.

20. 5 m³ of air at a pressure, p_1 , of 4 atm and at $t_1 = 60^\circ\text{C}$ are expanded to three times the initial volume and to a pressure of 1 atm. Evaluate the index of the polytropic, the expansion work, the quantity of heat exchanged and the change of internal energy in this process.

21. An elastic rod of length l is stretched by a force p . Determine the ratio λ_T/λ_S of the coefficients of isothermal and adiabatic linear expansion ($\lambda = l^{-1}dl/dp$).

22. Find the ratio of the magnetic susceptibilities dM/dH of a magnet for adiabatic and isothermal processes.

23. The heat released when water is formed from its elements is equal to $Q_1 = 68.4$ kcal/mole, and the molar heat of vaporization of water is $Q_2 = 9.5$ kcal/mole. Determine the heat produced when water vapour is formed from its elements.

24. In the complete combustion of a mole of methane to form carbonic acid and water, a quantity of heat $Q_1 = 211.9$ kcal is released. On the other hand when water is formed from its elements the quantity of heat released is $Q_2 = 68.4$ kcal/mole,

and in the complete combustion of carbon $Q_3 = 97$ kcal/mole. Determine the heat Q accompanying the generation of methane from solid carbon and gaseous hydrogen.

25. The heat Q of a reaction occurring at constant volume or at constant pressure depends on the temperature T . Determine $(\delta Q/\partial T)_V$ and $(\delta Q/\partial T)_P$. Find the variation of the heat of combustion of a mole of hydrogen to form water for an increase of temperature by 1°C .

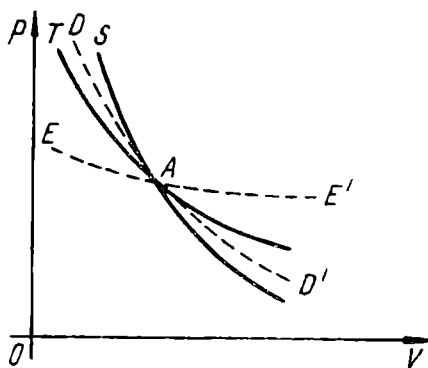


FIG. 5.

26. Through a point A on the work diagram V, p (Fig. 5) are drawn the isothermal T and the adiabatic S of an ideal gas. Show that an arbitrary polytropic process, represented on this diagram by the curve DAD' , occurs with a negative thermal capacity, while a process represented by such a curve as EAE' occurs with a positive thermal capacity.

27. Determine the conditions under which an adiabatic coincides with an isothermal.

CHAPTER III

THE SECOND LAW OF THERMODYNAMICS

§ 11. General features and initial formulation of the second law

In one and every system, as we have seen, the first law of thermodynamics establishes the existence of a single-valued parameter of state—the internal energy, that does not vary in the absence of external actions, whatever the processes inside the system.

The second law of thermodynamics, which we are now going to consider, establishes the existence in an arbitrary equilibrium system of a new single-valued parameter of state—the entropy, which, however, in contrast to internal energy, remains constant in isolated systems for and only for quasi-static processes and always increases in non-static processes.

Thus, if the first law is the law of conservation and transformation of energy (in its quantitative aspect), then the second law is the law of entropy.

Historically the discovery of the second law is connected with the analysis of the work of heat engines, which fact also determines the initial formulation of the law itself. The work of heat engines was firstly considered theoretically in 1824 by Sadi Carnot who, in his investigation “Considerations on the moving force of fire and on machines capable of developing these forces,” though proceeding from the “caloric” concept, proved nevertheless with complete rigour the theorem according to which the efficiency of heat engines working on a determined cycle (Carnot’s cycle) is independent of the substance that accomplishes this cycle. Later Clausius and B. Thompson, having rejected Carnot’s ideas on the caloric concept and having established anew the correctness of Carnot’s theorem, gave nearly at the same time a sound basis of the content of what is now the second law.

Just as the first law, the second law of thermodynamics is a generalization of experimental data. Practical experience gathered by man over many years has led him to ascertain certain regular features of the conversion of heat into work and work into heat (some true of

both “ordinary” and “non-ordinary” systems† and some specific of the ones or the others). As a result of an analysis of these regular features the second law of thermodynamics was formulated as the law of the existence of entropy and its never decreasing in isolated systems whatever the processes undergone by them. In order to arrive at such a formulation of the second law of thermodynamics, we shall assume as its initial formulation one that is directly connected with the regular features observed in the conversion of heat into work and work into heat. Here, owing to the rare occurrence of non-ordinary systems (they are almost exclusively systems of nuclear spins) we shall proceed from a formulation of the second law of thermodynamics that applies to ordinary systems, the ones occurring most often. Only in § 46 corresponding regular features will be shown to occur for spin systems and the same law of increasing entropy will be established. In the same section we shall also give an initial formulation of the second law of thermodynamics valid for both ordinary and non-ordinary systems.

As has already been pointed out in § 4, it follows from the definition of the concepts of heat and work that these two forms of transmission of energy considered in thermodynamics are not equivalent: whereas work can directly be converted into an increase of any form of energy, heat directly results (if not preliminarily converted into work) merely in an increase of the internal energy of a system. This lack of equivalence of heat and work would be of no importance if we could convert heat into work without any difficulties. However, as is shown by experiment, whereas in the conversion of work into heat the process can only be restricted by a variation of the thermodynamic state of the heat-receiving body (for example, in heating by friction or in electrical heating), in the conversion of heat into work, together with the cooling of the heat-giving body, there occurs a variation of the thermodynamic state of other bodies taking part in this process: either the working body in a non-closed process, or other bodies in a closed-cycle process, when these bodies are bound to receive from the working body a part of the heat received by it from the heater. In heat engines such “other bodies” are usually coolers.

A variation of the state of the working body (if the process is not a closed one) or the cession of heat by the working body to other bodies and a variation of the thermodynamic state of these bodies in a closed-cycle process of conversion of heat into work is called *com-*

† For a definition of “ordinary” and “non-ordinary” systems see § 4.

pensation. Experiment thus leads to the result that without compensation not a single calorie of heat could be converted into work. On the contrary, work can be converted into heat without any compensation whatsoever.

Such "inequality" of the conversion of heat into work compared with the conversion of work into heat results in a unilateralness of natural processes:† spontaneous processes in a closed system go in the direction of the vanishing of the potentially possible work. For example, no cases are observed in practice of spontaneous flow of heat from a cold body to a hot body whereas, on the contrary, when two bodies of different temperature are in thermal contact heat flows from the hot body to the cold one until their temperatures are equalized. Where there is a temperature difference between two bodies the possibility exists (see § 18) of obtaining work (potentially possible work); the spontaneous process occurring when such bodies are brought into contact goes in the direction of the vanishing of this possible work.

In actual practice, in designing heat engines, jet-propulsion engines, etc., these laws of nature are to be taken into account and the analysis of various kinds of physical phenomena is to be carried out on their basis.

Then the initial formulation of the second law of thermodynamics which expresses the laws of the conversion of heat into work and of work into heat (in the case of ordinary systems) will be the following: "*A perpetual motor of the second kind is impossible and this statement admits of no converse proposition.*"‡ This means that, while heat cannot be converted into work completely without compensation (a perpetual motor of the second kind is impossible), work can be completely converted into heat without any compensations whatsoever, since there would be no difficulties at all in constructing a machine the sole func-

† If the conversion of heat into work and that of work into heat were equivalent, i.e. if the conversion of work into heat were also bound to involve compensation, or else if the conversion of heat into work could occur without compensation, there would be no unilateralness of natural processes. In the case of a system of spins there occurs just the opposite "inequality": work cannot be converted into heat without a variation in the surrounding bodies, whereas heat can be converted into work without such a variation (see § 46).

‡ This is in contrast to the proposition of the impossibility of a perpetual motor of the first kind which does admit of a converse proposition (see p. 45), though this aspect of the proposition of the perpetual motor of the first kind is not stated explicitly in the formulation of the first law of thermodynamics, since it has no role in establishing the existence of the internal energy of a system as a single-valued function of its state, which is the content of the first law of thermodynamics. Similarly, for

tions of which were to be reduced to the expending of work and the heating of a reservoir (the impossibility of a converse proposition to that of a perpetual motor of the second kind).†

In other words, if heat is converted into work and, after a complete closed-cycle process, some body or various bodies have released a positive quantity of heat $Q = \oint \delta Q (\delta Q > 0)$ while a positive work equal to W has been accomplished, then we always have

$$Q \underset{\rightarrow}{>} W, \quad (3.A)$$

but if, on the contrary, work W ($W > 0$) is converted into heat Q , then we always have

$$W \underset{\rightarrow}{=} Q \quad (3.B)$$

the arrows underneath indicating the direction of the process.

As can be seen from the formulae shown, the second law of thermodynamics is the aggregate of two independent theses:

$$Q \underset{\rightarrow}{>} W \quad \text{and} \quad W \underset{\rightarrow}{=} Q. \quad (3.1)$$

As will be shown, the first thesis ($Q \underset{\rightarrow}{>} W$) leads, in the case of equilibrium systems, to establishing the existence of the absolute temperature and of a new single-valued parameter of state—the entropy. The first and second thesis of the second law of thermodynamics together establish the unilateral nature of the variation of entropy in natural processes in closed systems.

Thus, as will be shown in §§ 13 and 14, *the second law of thermodynamics expresses the law of the existence of entropy in every equilibrium system and of its never decreasing in isolated systems for any processes whatsoever.*

The first thesis of the second law of thermodynamics indicates the impossibility of converting heat into work without compensation by

establishing the existence of entropy, the statement of the impossibility of a converse proposition to the proposition of a perpetual motor of the second kind is also unnecessary. However, to establish later the second thesis of the second law of thermodynamics (the thesis of the growth of entropy) we must use the statement of the impossibility of a converse proposition to that of the perpetual motor of the second kind. In addition, as we now know, this statement is not always valid. All this leads to the necessity of explicitly stating the impossibility of conversion of the proposition of the perpetual motor of the second kind in the initial formulation of the second law of thermodynamics (for ordinary systems).

† Thus, while the first law of thermodynamics expresses the quantitative equivalence of heat and work, the second law of thermodynamics establishes their qualitative non-equivalence.

means of a closed-cycle process. The concept of compensation, as can be seen from its definition, contains two elements: the cession of a portion of heat by the working body to other bodies and the variation of the thermodynamic state of these other bodies in the conversion of heat into work in a closed-cycle process. In the case of ordinary systems, the ones occurring most often, these two compensation elements coincide, since the cession of a portion of heat by the working body to other bodies in a closed-cycle process is irretrievable and automatically involves a variation of the thermodynamic state of these other bodies. In the case of systems of spins these compensation elements, as we shall see, do not coincide, as a consequence of which the heat of some body can, by means of systems of spins, be entirely converted into work using a closed-cycle process, without any variation of the thermodynamic state of other bodies. However, such a conversion is necessarily accompanied by the cession of a portion of heat by the working body to other bodies. Just this common aspect (the common element of compensation) of the conversion of heat into work in ordinary systems and in systems of spins leads to the existence of entropy in equilibrium systems, whether ordinary or non-ordinary.

A device, the operation of which would result in the periodical generation of positive work, only at the expense of cooling a single body without any other variations in bodies, is called the Thomson-Planck perpetual motor of the second kind. When ordinary systems are used the Thomson-Planck perpetual motor of the second kind cannot be implemented, but in the presence of systems of spins such a motor is well possible. However, a device that would continuously convert the heat of a body into work without compensation, namely a perpetual motor of the second kind, is impossible even in the presence of systems of spins.† In this connexion, while in the case of ordinary systems the proposition of the perpetual motor of the second kind does not admit of conversion, in the case of systems of spins such a conversion is possible (see § 46).

We shall set ourselves the task of obtaining an analytical expression of the second law of thermodynamics with a view to its subsequent applications. Therefore we shall consider separately the second law of thermodynamics for equilibrium (quasi-static) processes and for non-equilibrium (non-static) processes.

† It is evident that the "perpetual motor of the second kind" and the "Thomson-Planck perpetual motor of the second kind" coincide in the case of ordinary systems.

At first, however, by proceeding from the second law of thermodynamics, we shall consider the classification of all processes into reversible and irreversible processes and shall establish how these processes are related to equilibrium and non-equilibrium processes.

§ 12. Reversible and irreversible processes

The second law of thermodynamics enables us to divide all processes into two classes: reversible and irreversible ones. There follows, in fact, from the second law of thermodynamics, in the first place, the impossibility of such processes as are necessarily accompanied by the conversion of heat into work without compensation (the non-compensated conversion of heat into work) and, in the second place, the possibility of the other processes that are not connected with such a conversion; this leads to dividing all processes that occur in a closed system into reversible and irreversible processes.

The process of transition of a system from a state 1 to a state 2 is called *reversible* if the opposite transition of the system from 2 to 1 is not connected with a non-compensated conversion of heat into work; on the contrary, the process of the transition of a system from 1 to 2 is called *irreversible* if the opposite transition of the system from 2 to 1 does involve a non-compensated conversion of heat into work. It is evident that every quasi-static process is reversible; in fact, the state in such a process at each instant is completely determined by the external parameters and temperature, and therefore by equilibrium variations of these parameters in the opposite direction the system will pass through all the states also in the opposite direction and will reach the initial state without causing any variations in the surrounding bodies.

In processes involving friction, as we have pointed out, work can be converted without compensation into heat; since the opposite transition of the system from the final to the initial state is connected with a non-compensated transition of heat into work, it follows, that processes involving friction are irreversible.†

† This is found to be in agreement with our conception of the nature of mechanical friction. Friction between two bodies in contact with each other is a consequence of the fact that the surfaces of those bodies are not absolutely smooth but are, to a greater or smaller degree, uneven; therefore, in order to displace one body with respect to the other, a certain *finite* effort is needed to overcome the forces caused by the unevenness of those surfaces.

A measure of the irreversibility of a process in a closed system (see § 16) is the variation of a new parameter of state—the entropy, the existence of which in an equilibrium system is established by the first thesis of the second law of thermodynamics on the impossibility of a perpetual motor of the second kind. The single-valuedness of this parameter of state results in the fact that every irreversible process is non-static†. The converse conclusion of the irreversibility of every non-static process cannot be derived from the second law of thermodynamics. It is shown by experiment that except for two non-static processes, known so far, superconductivity and superfluidity, all remaining non-static processes are irreversible.

As examples of irreversible processes we shall also cite the following ones:

1. The heat-transmission process in the presence of a finite temperature difference is irreversible, since the opposite transition is connected with the abstraction of a determined quantity of heat from a cold body, with its non-compensated conversion into work and with expenditure of the latter for increasing the energy of a hot body (see § 19). The irreversibility of this process can also be seen from the fact that it is non-static.

2. The expansion of a gas in a vacuum is irreversible since in such an expansion no work is accomplished, and to compress a gas in such a manner as to accomplish no work is impossible. The work executed in compressing a gas goes to heating it; for the gas temperature not to rise we need to remove heat from it, and in order that no variations be produced in the surrounding bodies, this heat must be converted into work, which is impossible without compensation.

3. The process of diffusion is irreversible. In fact, if in a vessel containing two different gases separated by a partition the partition is removed, then each gas will diffuse into the other. In order to separate the gases each of them must be compressed; for their temperature not to rise, heat must be removed from them, and in order that no variations shall occur in the surrounding world this heat must be converted into work without compensation, which is impossible.‡

† Concerning this, see § 16.

‡ On the reversible mixing of gases see problem no. 32.

§ 13. The second law of thermodynamics for quasi-static processes. Entropy and absolute temperature

It follows from the impossibility of a perpetual motor of the second kind (the first part of the second law of thermodynamics) that in the vicinity of each state of a thermally homogeneous† equilibrium system there exist states that cannot be reached by adiabatic means (*the principle of adiabatic unattainability* of Carathéodory).

In fact, let the system pass quasi-statically from the state 1 to the state 2, by receiving a positive quantity of heat $Q = \int \delta Q$ ($\delta Q > 0$) and accomplishing the work W_1 , then we have, according to the first law of thermodynamics,

$$Q = U_2 - U_1 + W_1. \quad (3.2)$$

A distinctive feature of the process considered is the invariability of the heat exchange ($\delta Q > 0$). In this connexion, during the whole course of the process positive heat is removed either from one and the same body or from various bodies. If this body is a thermostat, then the process 1-2 will be isothermal, but, if a system similar to the one studied (or several such systems) is taken as such a body, then the process will not be isothermal but some other process, though not an adiabatic process.

By assuming that the system can pass adiabatically from the state 2 to the state 1 on accomplishing the work W_2 , we have

$$0 = U_1 - U_2 + W_2. \quad (3.3)$$

By adding (3.2) and (3.3) we shall obtain that during the whole circular process the work $W_1 + W_2$ has been accomplished at the expense of a non-compensated conversion of heat Q :

$$Q = W_1 + W_2 > 0. \quad (3.4)$$

Since by the second law of thermodynamics (3.1) (its first part) such a process is impossible, it follows that the state 1 is adiabatically unattainable from the state 2.

The physical meaning of the principle of adiabatic unattainability consists in the statement that in every equilibrium system there exists a certain new parameter of state S which does not vary in quasi-static adiabatic processes. We can easily convince ourselves of this, by proceeding from the following considerations.

It can easily be observed that the thesis of the existence in every equilibrium system of a temperature t can be formulated in the form of a principle of isothermal unattainability: in the vicinity of each state

† A thermally homogeneous system is a system all parts of which have the same temperature (i.e. a system in which no thermally impermeable [adiabatic] partitions exist). The principle of adiabatic unattainability is, generally speaking, not valid for a thermally inhomogeneous system (see problem no. 34).

of an equilibrium system there exist such states that are unattainable isothermally. In fact from a state of the system at a temperature $t = t_1$ it is impossible isothermally to take the system to a state with a temperature $t = t_2$. Similarly to this, the impossibility of the quasi-static adiabatic reduction of a system from a state 1 to a certain state 2 means that in the state 1 the system has a value equal to S_1 of a certain parameter S and a value $S = S_2$ in the state 2, the parameter S being one that does not vary in quasi-static adiabatic processes. And, just as in an isothermal process $t = \text{const}$, in an adiabatic process $S = \text{const}$.

As will be shown in the following section, this result of the principle of adiabatic unattainability can be obtained more rigorously on establishing, on the basis of the same principle, that *the differential Pfaffian form for a quasi-static element of heat* (2.15), which by the first law of thermodynamics is not a total differential, *will always have an integrating factor (or divisor) which depends only on the temperature of the system* $\varphi(t)$: $\delta Q/\varphi(t) = dS$ (where dS is the total differential of a certain function S), in which connection although the form of the function $\varphi(t)$ depends on the choice of the empirical temperature t , the numerical value of this function does not depend on the choice of the empirical temperature (see § 14).

On denoting $\varphi(t) = T$ we shall obtain

$$\frac{\delta Q}{T} = dS. \quad (3.5)$$

Physically (3.5) denotes the existence in an equilibrium system of a new function of state S called *entropy* and of a temperature T which does not depend on the thermometric substance (*absolute temperature*).

From the impossibility of a perpetual motor of the second kind there also follows that this new parameter of state—the entropy S —is a single-valued parameter of state. This means that $\oint \delta Q/T$ is equal to zero for an arbitrary closed-cycle quasi-static process. If this were not so, we could by means of a periodically acting machine obtain, after each cycle, work W only at the expense of cooling a single body—a thermostat. In fact, since by the first law of thermodynamics

$$W = Q = \oint \delta Q, \quad (3.C)$$

and, according to (3.5)

$$\oint \delta Q = \oint T dS, \quad (3.D)$$

then

$$W = \oint T dS = T \oint dS \neq 0, \quad (3.E)$$

if $\oint dS \neq 0$.

The impossibility of a perpetual motor of the second kind leads to

$$\oint dS = 0 \quad (3.6)$$

in an arbitrary closed-cycle process, which fact expresses the single-valuedness of entropy. It can also be seen from what has been expounded that the work in an isothermal closed-cycle process is equal to zero.†

The thesis of the existence in an equilibrium system of a new single-valued function of state, the entropy S , is the content of the second law of thermodynamics for quasi-static processes.

Mathematically the second law of thermodynamics for quasi-static processes will be described by the equation

$$\frac{\delta Q}{T} = dS \quad (3.F)$$

or

$$\delta Q = T dS. \quad (3.7)$$

This expression for an element of quantity of heat has the same form as the expression (1.3) for the element of work, the absolute temperature being the intensive parameter of heat transmission (the thermal generalized force) while the entropy S is the extensive parameter of heat transmission (the generalized coordinate). As we have already pointed out in § 4, the similarity of the expressions for δQ and δW is due to the kindred nature of these quantities: both represent quantities of energy received by the system.

The integral equation of the second law of thermodynamics for quasi-static closed-cycle processes is *Clausius' equality*.

$$\oint \frac{\delta Q}{T} = 0. \quad (3.8)$$

§ 14. Mathematical justification for the existence of entropy and absolute temperature

We shall now set ourselves the task of justifying mathematically the results obtained in § 13: that from the adiabatic unattainability there follows the existence of an integrating factor (or divisor) for a quasi-static element of heat δQ , and that among these integrating factors μ there exists one that depends only on temperature $\mu = \varphi(t)$,

† When non-static processes are used the work W during a cycle for a single heat source can be negative (see problem no. 44).

the numerical value of this function being independent of the choice of the empirical temperature t , though the form of the function $\varphi(t)$ is connected with such a choice.

1. *Holonomicity of the differential form δQ*

As we have already pointed out,[†] the expression for an element of quantity of heat has the form of a linear differential in the total differentials of the independent variables t, a_1, a_2, \dots, a_n , i.e. Pfaff's form

$$\delta Q = C_{a_1, a_2, \dots, a_n} dt + l_{a_1} da_1 + l_{a_2} da_2 + \dots + l_{a_n} da_n. \quad (3.9)$$

All Pfaffian forms

$$\delta \Pi_m = X_1 dx_1 + X_2 dx_2 + \dots + X_m dx_m \quad (3.10)$$

(where x_1, x_2, \dots, x_m are independent variables and X_1, X_2, \dots, X_m are functions of these variables) are divided into two classes differing substantially from each other in various properties.

One class of Pfaffian forms are either the total differentials of certain functions of the independent variables or are proportional to some total differential, i.e. have an integrating factor $\mu(x_1, x_2, \dots, x_m)$, so that after multiplying $\delta \Pi_m$ by this factor the expression obtained is the total differential of a certain function $\Phi(x_1, x_2, \dots, x_m)$:

$$\begin{aligned} \mu(x_1, x_2, \dots, x_m) (X_1 dx_1 + X_2 dx_2 + \dots + X_m dx_m) = \\ = d\Phi(x_1, x_2, \dots, x_m); \end{aligned} \quad (3.G)$$

whereas the other Pfaffian forms in addition to not being total differentials are not proportional to any total differential whatsoever, i.e. do not have an integrating factor.

Pfaffian forms having an integrating factor are called holonomic, and those having no integrating factor are called non-holonomic.

If the number of variables m equals 2, there is always an integrating factor, i.e. Pfaffian forms of two independent variables are always holonomic (see problem no. 37); in the case $m > 2$, however, Pfaffian forms can be either holonomic or non-holonomic: all depends on the coefficients X_1, X_2, \dots, X_m qualifying the differentials of the independent variables x_1, x_2, \dots, x_m .

It is easy to find the conditions that these coefficients must satisfy in order that a Pfaffian form be holonomic. For $m = 3$ a Pfaffian form has the form

$$\delta \Pi_3 = X_1 dx_1 + X_2 dx_2 + X_3 dx_3. \quad (3.11)$$

[†] See § 7, the formula (2.15).

If $\delta\Pi_3$ is holonomic then

$$\begin{aligned} \mu(x_1, x_2, x_3)(X_1 dx_1 + X_2 dx_2 + X_3 dx_3) &= d\Phi(x_1, x_2, x_3) = \\ &= \frac{\partial\Phi}{\partial x_1} dx_1 + \frac{\partial\Phi}{\partial x_2} dx_2 + \frac{\partial\Phi}{\partial x_3} dx_3, \end{aligned} \quad (3.H)$$

whence

$$\frac{\partial\Phi}{\partial x_1} = \mu X_1, \quad \frac{\partial\Phi}{\partial x_2} = \mu X_2, \quad \frac{\partial\Phi}{\partial x_3} = \mu X_3, \quad (3.J)$$

and, since, for a given pair of variables, mixed derivatives are independent of the order of differentiation, then

$$\begin{aligned} \frac{\partial}{\partial x_2}(\mu X_1) &= \frac{\partial}{\partial x_1}(\mu X_2), \\ \frac{\partial}{\partial x_3}(\mu X_2) &= \frac{\partial}{\partial x_2}(\mu X_3), \\ \frac{\partial}{\partial x_1}(\mu X_3) &= \frac{\partial}{\partial x_3}(\mu X_1). \end{aligned} \quad (3.K)$$

By eliminating from these equations the function $\mu(x_1, x_2, x_3)$, we shall multiply the first equation by X_1 the second by X_2 and the third by X_3 and after this we shall add them up. We shall then obtain the necessary condition of holonomicity of the Pfaffian form (3.11)

$$X_1 \left(\frac{\partial X_3}{\partial x_2} - \frac{\partial X_2}{\partial x_3} \right) + X_2 \left(\frac{\partial X_1}{\partial x_3} - \frac{\partial X_3}{\partial x_1} \right) + X_3 \left(\frac{\partial X_2}{\partial x_1} - \frac{\partial X_1}{\partial x_2} \right) = 0, \quad (3.12)$$

or, more briefly,

$$(Z, \text{rot } Z) = 0, \quad (3.13)$$

where Z is a vector of components X_1, X_2 and X_3 .

This condition is not only necessary but also sufficient: when it is satisfied the Pfaffian form (3.11) is holonomic.

In the general case of an arbitrary number of variables ($m > 3$) for the Pfaffian form (3.10) to be holonomic it is necessary that the following identity

$$(Z, \text{rot } Z) = 0, \quad (3.L)$$

be satisfied for any three of the functions X_i , Z being a vector of components equal to three of these functions.

By equating a Pfaffian form to zero we shall obtain Pfaff's equation.

$$\delta\Pi_3 = 0 \quad (3.14)$$

for a holonomic form (3.11), i.e. for $\mu\delta H_3 = d\Phi(x_1, x_2, x_3)$, has an integral in the form of a single-parameter family of surfaces in the x_1, x_2, x_3 space

$$\Phi(x_1, x_2, x_3) = C. \quad (3.15)$$

Using a thermodynamic analogy, such surfaces are called adiabatic†. By imposing (additional) requirements on the coefficients X_1, X_2 and X_3 , we obtain surfaces that do not intersect each other.‡

In this case, by moving from a given point on any one adiabatic surface we can never go beyond the boundary of the integral surface passing through this point. In this case, therefore, in the vicinity of every point there exist such points (situated on other integral surfaces) that are adiabatically unattainable (i.e. points that cannot be reached without leaving the given integral surface).

It can easily be shown that the converse conclusion is also true: if in the vicinity of a given state of the system there exist such states that are unattainable from it by means of Pfaff's equation $\delta H_3 = 0$, then this equation is holonomic.

In fact, if in the vicinity of each point there exist such points that are unattainable from it by means of Pfaff's equation (3.14)

$$\delta H_3 = X_1 dx_1 + X_2 dx_2 + X_3 dx_3 = 0, \quad (3.M)$$

then this means that the equation (3.14) engenders such a connexion between the variables x_1, x_2, x_3 as represents a single-parametric family of non-intersecting surfaces $\Phi(x_1, x_2, x_3) = C$: in this case, in fact, from an arbitrary point on any one adiabatic surface (for $C = C_1$) we can reach no point on the other surfaces ($C = C_2, C_3, \dots$).

† Pfaff's equation $\delta H_m = 0$ is similar to the adiabaticity condition $\delta Q = 0$.

‡ This is always the case if at least one of the coefficients X_1, X_2, X_3 reduces to zero at no point of the region D of variation of the independent variables x_1, x_2, x_3 . In the opposite case, adiabatics can intersect each other, and therefore the function $\Phi(x_1, x_2, x_3)$ will not be single-valued. The absence of intersections of the individual surfaces $\Phi(x_1, x_2, x_3) = C$ expresses the adiabatic unattainability, but does not by itself guarantee the single-valuedness of the function $\Phi(x_1, x_2, x_3)$. Cases are possible when none of the coefficients X_1, X_2, X_3 reduce to zero at any one point of the region D (and therefore the individual surfaces of the family $\Phi(x_1, x_2, x_3) = C$ do not intersect each other) but nevertheless the function $\Phi(x_1, x_2, x_3)$ is not single-valued. This occurs when the space of states is doubly connected.

In the case of a Pfaffian form for δQ the space of states of real systems is always simply connected since, as we have shown in § 13, the second law of thermodynamics enables us to prove the single-valuedness of entropy.

Thus a differential relation between the variables x_1, x_2, x_3 is determined by the equation

$$\frac{\partial \Phi}{\partial x_1} dx_1 + \frac{\partial \Phi}{\partial x_2} dx_2 + \frac{\partial \Phi}{\partial x_3} dx_3 = 0 \quad (3.15a)$$

and therefore the coefficients qualifying dx_1 in (3.M) and (3.15a) are proportional to each other

$$\begin{aligned} \mu (X_1 dx_1 + X_2 dx_2 + X_3 dX_3) &= \\ &= \frac{\partial \Phi}{\partial x_1} dx_1 + \frac{\partial \Phi}{\partial x_2} dx_2 + \frac{\partial \Phi}{\partial x_3} dx_3 = d\Phi (x_1, x_2, x_3), \end{aligned} \quad (3.N)$$

which indicates the holonomicity of $\delta \Pi_3$.†

In the case of a non-holonomic Pfaffian form when the condition of total integrability (3.13) is not satisfied, Pfaff's equation (3.14) has no integrals in the form of a family of surfaces; in this case the integral variety of Pfaff's equation is a unidimensional variety (i.e. a variety of lines in the x_1, x_2, x_3 space) depending on an arbitrary function and on a single arbitrary parameter C :

$$\psi(x_1, x_2, x_3) = 0, \quad x_2 = \varphi(x_1, C), \quad (3.16)$$

where φ is an arbitrary function. Owing to this arbitrary function occurring in the equation of an integral line, we can always draw a line through any two points of the x_1, x_2, x_3 space (see problem no. 38).

Thus, in this case, we can go adiabatically ($\delta \Pi_3 = 0$) from each point to any other point; i.e. when the Pfaffian form is non-holonomic no adiabatically unattainable points exist.

If we return now to the differential Pfaffian form for an element of quantity of heat (3.9) we observe that, since the impossibility of a perpetual motor of the second kind leads to the existence of adiabatically unattainable states in a neighbourhood of each state, then it follows that this form is always holonomic, i.e. δQ has always an integrating factor.

2. The existence of entropy

We shall show that among the integrating factors of the expression δQ there is such a factor as depends only on temperature and determines the entropy of the system.

Let there be two sub-systems that are found in thermal equilibrium. The state of the first sub-system is determined by the parameters

† This proposition is similarly shown for the general case $m > 3$.

t, a_1, a_2, \dots, a_n , the state of the second sub-system by the parameters t, b_1, b_2, \dots, b_m , and the state of the whole system by the parameters $t, a_1, a_2, \dots, a_n, b_1, b_2, \dots, b_m$.

Suppose that in a certain quasi-static process the system as a whole receives a quantity of heat δQ , the quantities δQ_1 and δQ_2 being the shares of each sub-systems, so that

$$\delta Q = \delta Q_1 + \delta Q_2. \quad (3.17)$$

According to what has been shown, all these elements of heat are holonomic, and therefore they can be represented in the form

$$\delta Q_1 = \lambda_1 d\sigma_1, \quad \delta Q_2 = \lambda_2 d\sigma_2, \quad \lambda Q = \lambda d\sigma, \quad (3.18)$$

where $\lambda_1 = \lambda_1(t, a_1, \dots, a_n)$, $\lambda_2 = \lambda_2(t, b_1, \dots, b_m)$ and $\lambda = \lambda(t, a_1, \dots, a_n, b_1, \dots, b_m)$ are the corresponding integrating divisors.

The functions σ_1 and σ_2 are functions of state respectively of the first and second sub-system. They can be taken as independent variables of each of these sub-systems, for example in lieu of the parameter a_1 of the first sub-system and of the parameter b_1 of the second sub-system, so that

$$\begin{aligned} \lambda_1 &= \lambda_1(t, \sigma_1, a_2, \dots, a_n), \\ \lambda_2 &= \lambda_2(t, \sigma_2, b_2, \dots, b_m), \\ \lambda &= \lambda(t, \sigma_1, \sigma_2, a_2, \dots, a_n, b_2, \dots, b_m), \\ \sigma &= \sigma(t, \sigma_1, \sigma_2, a_2, \dots, a_n, b_2, \dots, b_m) \end{aligned} \quad (3.0)$$

and

$$d\sigma = \frac{\partial \sigma}{\partial t} dt + \frac{\partial \sigma}{\partial \sigma_1} d\sigma_1 + \frac{\partial \sigma}{\partial \sigma_2} d\sigma_2 + \sum_{i=2}^n \frac{\partial \sigma}{\partial a_i} da_i + \sum_{k=2}^m \frac{\partial \sigma}{\partial b_k} db_k. \quad (3.19)$$

On the other hand, by substituting (3.18) in (3.17) we shall obtain

$$d\sigma = \frac{\lambda_1}{\lambda} d\sigma_1 + \frac{\lambda_2}{\lambda} d\sigma_2. \quad (3.20)$$

By comparing (3.19) and (3.10) we find that $\partial \sigma / \partial \sigma_1 = \lambda_1 / \lambda$, $\partial \sigma / \partial \sigma_2 = \lambda_2 / \lambda$ and that the coefficients qualifying $dt, da_2, \dots, da_n, db_2, \dots, db_m$ are equal to zero. Hence by equating the mixed derivatives obtained from (3.19) we shall have

$$\frac{\partial}{\partial t} \left(\frac{\lambda_1}{\lambda} \right) = 0, \quad \frac{\partial}{\partial t} \left(\frac{\lambda_2}{\lambda} \right) = 0, \quad (3.21)$$

$$\frac{\partial}{\partial a_i} \left(\frac{\lambda_1}{\lambda} \right) = 0, \quad \frac{\partial}{\partial a_i} \left(\frac{\lambda_2}{\lambda} \right) = 0, \quad (3.22)$$

$$\frac{\partial}{\partial b_k} \left(\frac{\lambda_1}{\lambda} \right) = 0, \quad \frac{\partial}{\partial b_k} \left(\frac{\lambda_2}{\lambda} \right) = 0 \quad (3.23)$$

$$(i = 2, \dots, n; \quad k = 2, 3, \dots, m).$$

It follows from (3.21) that if the parameter t occurs in the expressions for λ_1 , λ_2 and λ it can only occur in the form of one and the same function $\varphi(t)$, so that

$$\left. \begin{aligned} \lambda_1 &= \varphi(t) \cdot f_1(\sigma_1, a_2, \dots, a_n), \\ \lambda_2 &= \varphi(t) \cdot f_2(\sigma_2, b_2, \dots, b_m), \\ \lambda &= \varphi(t) \cdot f(\sigma_1, \sigma_2, a_2, \dots, a_n, b_2, \dots, b_m). \end{aligned} \right\} \quad (3.24)$$

Since λ_1 does not depend on b_k and λ_2 does not depend on a_i , then it follows from (3.22) and (3.23) that λ does not depend on a_i and b_k , λ_1 does not depend on a_i , and λ_2 does not depend on b_k .

Thus we have from (3.24) that

$$\left. \begin{aligned} \lambda_1 &= \varphi(t) \cdot f_1(\sigma_1), \\ \lambda_2 &= \varphi(t) \cdot f_2(\sigma_2), \\ \lambda &= \varphi(t) \cdot f(\sigma_1, \sigma_2). \end{aligned} \right\} \quad (3.25)$$

The functions, $f_1(\sigma_1)$, $f_2(\sigma_2)$ and $f(\sigma_1, \sigma_2)$ occurring here are arbitrary since, as is known from mathematics, if there is but one integrating divisor λ_1 of a differential form δQ_1 , then the product of λ_1 by an arbitrary function $\psi(\sigma_1)$ will also be an integrating divisor.†

It follows from this that in the infinite set of integrating divisors there are also such ones for which the arbitrary functions $f_1(\sigma_1)$ and $f_2(\sigma_2)$ are equal to unity, i.e. there are divisors that depend only on temperature

$$\lambda_1 = \lambda_2 = \varphi(t); \quad (3.P)$$

in this connexion the integrating divisor λ will also be equal to $\varphi(t)$

$$\lambda = \lambda_1 = \lambda_2 = \varphi(t). \quad (3.26)$$

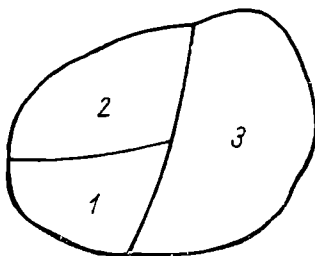


FIG. 6.

† This is easily verified by proceeding from the following considerations: if $\delta Q/\lambda_1 = d\sigma_1$ then $\delta Q/\lambda_1 \Psi(\sigma_1) = d\sigma_1/\Psi(\sigma_1) = d\bar{\sigma}_1$, where $\bar{\sigma}_1 = \int d\sigma_1/\Psi(\sigma_1)$; therefore $\lambda_1 = \lambda_1 \Psi(\sigma_1)$ is also an integrating divisor.

In fact, let us consider three sub-systems (Fig. 6) that are found in thermal equilibrium; according to what has been proved we have for each system pair

$$\lambda_1 = \lambda_2 = \varphi(t); \quad \lambda_2 = \lambda_3 = \varphi(t); \quad \lambda = \lambda_3 = \varphi(t) \quad (3.Q)$$

and therefore $\lambda_1 = \lambda_2 = \lambda = \varphi(t)$ (λ corresponds to the systems 1 and 2 taken as a whole).

The function S_1 defined by the equation

$$\frac{\delta Q_1}{\varphi(t)} = dS_1, \quad (3.R)$$

is called the entropy of the first system and the function S_2 , defined by the equation

$$\frac{\delta Q_2}{\varphi(t)} = dS_2, \quad (3.S)$$

is called the entropy of the second system.

On dividing (3.17) by (3.26) we shall obtain

$$\frac{\delta Q}{\varphi(t)} = dS_1 + dS_2 = d(S_1 + S_2) = dS, \quad (3.T)$$

where $S = S_1 + S_2$ is the entropy of the whole system, equal to the sum of the entropies of the individual sub-systems. *As can be seen from its definition, the entropy is an additive quantity proportional to the number of particles of the system.*

Thus it has been shown that among the integrating divisors of an element of heat δQ there is one, $\varphi(t)$, that depends only on the temperature t and is one and the same for arbitrary systems that are found in thermal equilibrium.

3. The absolute thermodynamic scale of temperature

The empirical temperature t that has been used by us until now has been defined on the basis of a variation (for example, the expansion) of some parameter of one or other thermometric substance—mercury, alcohol etc. As we have already pointed out, thermometers with different thermometric substances will indicate a different temperature at all conditions other than the fixed points 0 and 100°C. This indicates particularly clearly the arbitrariness and inadequacy of such a definition of temperature as an objective measure of the intensity of thermal motion.

The second law of thermodynamics eliminates this shortcoming and gives us the possibility of establishing an absolute thermodynamic scale independent of the thermometric substance. Indeed, as the integrating divisor $\varphi(t)$ for an element of heat δQ is determined only by the temperature, it can serve as a measure of temperature. The temperature $T = \varphi(t)$ is an absolute temperature since, as we shall show, though the form of the function $\varphi(t)$ does depend on the choice of the empirical temperature, the numerical value of this function does not depend on such a choice.

Let us find the connexion between absolute and empirical temperature determined on the basis of some thermodynamic process. Let the state of a simple system be determined by an external parameter a and by the absolute temperature $T = \varphi(t)$, the empirical temperature t being measured according to some parameter of a certain thermometric substance. Then, according to the first law of thermodynamics

$$\delta Q = dU + A da, \quad (3.U)$$

and according to the second law of thermodynamics

$$\frac{\delta Q}{T} = dS \quad (3.V)$$

and therefore

$$\frac{\left(\frac{\partial U}{\partial T}\right)_a dT + \left[\left(\frac{\partial U}{\partial a}\right)_T + A\right] da}{T} = \left(\frac{\partial S}{\partial T}\right)_a dT + \left(\frac{\partial S}{\partial a}\right)_T da, \quad (3.W)$$

whence

$$\left(\frac{\partial S}{\partial T}\right)_a = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_a, \quad \left(\frac{\partial S}{\partial a}\right)_T = \frac{1}{T} \left[\left(\frac{\partial U}{\partial a}\right)_T + A\right] \quad (3.X)$$

and

$$\frac{\partial}{\partial a} \left\{ \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_a \right\} = \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left[\left(\frac{\partial U}{\partial a}\right)_T + A\right] \right\}, \quad (3.Y)$$

or

$$T \left(\frac{\partial A}{\partial t}\right)_a = \left(\frac{\partial U}{\partial a}\right)_T + A. \quad (3.27)$$

As $T = \varphi(t)$, then $t = \psi(T)$ and

$$T \left(\frac{\partial A}{\partial t}\right)_a \cdot \frac{dt}{dT} = \left(\frac{\partial U}{\partial a}\right)_t + A, \quad (3.Z)$$

whence

$$\frac{dT}{T} = \frac{\left(\frac{\partial A}{\partial t}\right)_a dt}{\left(\frac{\partial U}{\partial a}\right)_t + A}. \quad (3.AA)$$

After integrating we obtain

$$\ln \frac{T}{T_0} = \int_{t_0}^t \frac{\left(\frac{\partial A}{\partial t}\right)_a dt}{\left(\frac{\partial U}{\partial a}\right)_t + A} = I, \quad \frac{T}{T_0} = e^I \quad (3.AB)$$

and

$$T = T_0 e^I, \quad (3.28)$$

where T and T_0 are values of temperature according to an absolute scale corresponding to the empirical temperatures t and t_0 respectively. The choice of T_0 determines the magnitude of the degrees.

It can be seen from the expression (3.28) that in the quasi-static transition of a system from one state to another the absolute temperature T cannot change its sign: it is either always positive or always negative. To prove the positiveness or negativeness of the absolute temperature is impossible. The sign of the absolute temperature is determined by an additional condition connected with defining which temperature is larger and which is smaller: it is assumed that when a body receives heat for constant external parameters its temperature increases, i.e. it is assumed that the thermal capacity $C_a = (\partial U / \partial T)_a$ is positive. We shall see in § 31 that this additional condition leads to a positive absolute temperature ($T > 0$).

If we assume the absolute temperature T to be positive (in accordance with the condition assumed† for determining which temperature is larger and which smaller), we arrive at the conclusion that ordinary systems cannot have negative absolute temperatures.

The formula (3.28) for the determination of the temperature T can also be represented in a somewhat different form. For an empirical temperature t_1 the absolute temperature T_1 is equal to

$$T_1 = T_0 e^{I_1}, \quad (3.AC)$$

whence

$$T_1 - T_0 = T_0 (e^{I_1} - 1), \quad (3.29)$$

† This additional condition leads to the formulation of the second law of thermodynamics in the case of non-static processes in adiabatic systems as *the law of increasing entropy* (see § 16).

where

$$I_1 = \int_{t_0}^t \frac{\left(\frac{\partial A}{\partial t}\right)_a dt}{\left(\frac{\partial U}{\partial a}\right)_t + A}. \quad (3. AD)$$

Let us divide (3.28) by (3.29); then we shall obtain

$$\frac{T}{T_1 - T_0} = \frac{e^I}{e^{I_1} - 1}, \quad (3. AE)$$

whence

$$T = (T_1 - T_0) \cdot \frac{e^I}{e^{I_1} - 1}. \quad (3. 30)$$

We shall choose the scale in such a manner that the difference between the fixed points $t_1 - t_0 = 100^\circ\text{C}$ shall correspond to the difference $T_1 - T_0 = 100^\circ\text{K}$. Then

$$T = 100 \frac{e^I}{e^{I_1} - 1}. \quad (3.31)$$

This formula enables us to determine the absolute temperature T from a given empirical temperature t determined on the basis of some property of some or other thermometric substance.

We shall show now that the value of the absolute temperature T in a given state does not depend on the choice of the thermometric substance. Let the state of a certain system be characterized by the empirical temperature t and, in addition, by another empirical temperature, τ , which is connected with the previous one by the relation $\tau = \tau(t)$. The absolute temperature Θ determined by means of the empirical temperature τ will be

$$\Theta = 100 \frac{e^{I_\tau}}{e^{I_{1\tau}} - 1}, \quad (3. AF)$$

(using the same difference $\theta_1 - \theta_0 = 100$ between the fixed points), where

$$I_\tau = \int_{\tau_0}^{\tau} \frac{\left(\frac{\partial A}{\partial \tau}\right)_a d\tau}{\left(\frac{\partial U}{\partial a}\right)_\tau + A} = \int_{t_0}^t \frac{\left(\frac{\partial A}{\partial t}\right)_a \frac{dt}{d\tau} d\tau}{\left(\frac{\partial U}{\partial a}\right)_t + A} = I, \quad (3. AG)$$

$$I_{1\tau} = \int_{\tau_0}^{\tau_1} \frac{\left(\frac{\partial A}{\partial \tau}\right)_a d\tau}{\left(\frac{\partial U}{\partial a}\right)_\tau + A} = \int_{t_0}^{t_1} \frac{\left(\frac{\partial A}{\partial t}\right)_a \frac{dt}{d\tau} d\tau}{\left(\frac{\partial U}{\partial a}\right)_t + A} = I_1,$$

and therefore

$$\Theta = T, \quad (3.AH)$$

i.e. the temperature according to an absolute scale does not depend on the choice of the thermometric substance.

We can take, therefore, for such a body an ideal gas that is found under the action of uniform pressure $A = p$, $a = V$. For an ideal gas $p = p_0(1 + \alpha t)$ (for $V = \text{const}$), $\alpha = 1/273.16$, t is the temperature according to the Celsius scale and

$$\left(\frac{\partial U}{\partial V}\right)_t = 0. \quad (3.AJ)$$

In this case the integrals I and I_1 are equal to

$$I = \int_{t_0}^t \frac{\left(\frac{\partial p}{\partial t}\right)_V dt}{\left(\frac{\partial U}{\partial V}\right)_t + p} = \int_{t_0}^t \frac{\alpha dt}{1 + \alpha t} = \ln \frac{1 + \alpha t}{1 + \alpha t_0}, \quad (3.AK)$$

$$I_1 = \ln \frac{1 + \alpha t_1}{1 + \alpha t_0}.$$

By substituting them in (3.31) we shall obtain

$$T = 100 \frac{1 + \alpha t}{\alpha (t_1 - t_0)}, \quad (3.AL)$$

and since $t_1 - t_0 = 100^\circ\text{C}$, then

$$T = \frac{1}{\alpha} + t = 273.16 + t. \quad (3.AM)$$

The absolute zero $T = 0^\circ\text{K}$ in the Celsius scale is equal to $t' = -273.16^\circ\text{C}$.

With the choice made by us of the value 100 for the difference of the absolute temperatures, $T_1 - T_0$, corresponding to the fixed points, i.e. with the choice of the Celsius degree as the measurement unit, the absolute temperature coincides with the gas temperature measured on the Kelvin scale.

§ 15. The fundamental equation of thermodynamics for quasi-static processes. The evaluation of entropy

The second law of thermodynamics for quasi-static processes establishes the existence of a new single-valued parameter of state—the entropy. Let us discuss the physical meaning of this function of state.

The equation of the second law of thermodynamics for quasi-static processes is

$$\delta Q = T dS. \quad (3.7)$$

By combining this equation with the equation of the first law of thermodynamics

$$\delta Q = dU + \sum_i A_i da_i, \quad (3.AN)$$

we shall obtain *the basic equation of thermodynamics for quasi-static processes*

$$T dS = dU + \sum_i A_i da_i, \quad (3.32)$$

which is the initial equation in the study of equilibrium processes.

From this equation we find a general expression for the variation of entropy in the quasi-static transition of a system from one state to another

$$S_2 - S_1 = \int_1^2 \frac{dU + \sum A_i da_i}{T}, \quad (3.33)$$

which shows that the basic equation (3.32) does not enable us to evaluate the absolute value of entropy: we can only determine a variation of entropy but not entropy itself. In this connexion in order to evaluate $S_2 - S_1$ we need to know the thermic and caloric equations of state

$$\begin{aligned} A_i &= A_i(T, a_1, \dots, a_n) \quad (i = 1, 2, \dots, n), \\ U &= U(T, a_1, \dots, a_n). \end{aligned} \quad (3.AO)$$

As these equations are known for an ideal gas: $pV = RT$ and $U = C_v T + U_0$ (for a monatomic ideal gas), we find for a mole of ideal gas

$$S_2 - S_1 = \int_1^2 \frac{C_v dT + p dV}{T} = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1}, \quad (3.34)$$

or

$$S = C_v \ln T + R \ln V + S_0, \quad (3.35)$$

where the constant S_0 is equal to

$$S_0 = S_1 - C_v \ln T_1 - R \ln V_1. \quad (3.36)$$

For ν moles of an ideal gas the entropy is equal to

$$S = \nu (C_v \ln T + R \ln V + S_0). \quad (3.37)$$

This expression for S in a particular case shows the additivity of entropy, and its proportionality to the number of particles of the system.

It can be seen from (3.37) that the entropy is evaluated on the basis of the first and second laws of thermodynamics except for a constant, νS_0 , which depends on the number of moles of the gas and, therefore, on the number of particles.

If there is a mixture of ideal gases, we can by means of semi-permeable diaphragms separate reversibly this mixture into its components without communicating heat and without expenditure of work and, therefore, without a variation of the entropy of the system (see problem no. 32). A consequence of this is Gibbs' theorem on the entropy of a mixture of ideal gases: the entropy of a mixture of ideal gases is equal to the sum of the entropies of the two gases separately, evaluated on the assumption that each of them occupies the whole volume of the mixture.

This theorem is not valid for a mixture of several portions of one and the same gas. If we ignore this fact we are led to the so-called Gibbs' paradox consisting in that a variation of entropy in diffusion must occur not only in the case of different gases but also in self-diffusion, when before diffusion (which begins after the removal of a diaphragm between two halves of a vessel) one and the same gas was found in both these halves and when no thermodynamic process occurs in the system.

Gibbs' paradox is automatically clarified if, according to the second law of thermodynamics, we supplement Gibbs' theorem with the statement that in the case of identical ideal gases the entropy of a mixture of such gases is equal to the sum of the entropies of these gases when each of them occupies the entire volume of the mixture minus the quantity $2\nu R \ln 2$ (ν is the number of moles in each part). (For a more detailed discussion of this see problem no. 39, where it is shown that the widely accepted opinion, according to which it is impossible to resolve fully Gibbs' paradox within the limits of thermodynamics, is incorrect.)

¶ We shall discuss now the problem of the physical meaning of entropy. The single-valued parameter of state, the entropy, the existence of which in an equilibrium system is established by the second law of thermodynamics, is not an intuitive quantity: it can be evaluated but cannot be directly measured similarly to temperature or volume—no "entropimeter" is available.

The physical meaning of entropy can be clarified both by an analysis

of quasi-static processes and in the study of non-static processes; the deeper thermodynamic meaning of entropy is revealed in an analysis of non-static processes. This meaning consists in that the variation of entropy is a measure of the irreversibility of processes in a closed system and characterizes the direction of natural processes. Of this more will be said in the next section.

In an analysis of quasi-static processes the concept of entropy can be to some extent elucidated by proceeding from the following considerations which clarify the meaning of the equation

$$dS = \frac{\delta Q}{T}, \quad (3.AP)$$

defining the differential of entropy.

The first law of thermodynamics establishes that an element of heat δQ is not a total differential (see problem no. 15). The physical meaning of this statement consists in that the quantity of heat that is needed in the transition of a system from one state to another depends on the path (i.e. on the conditions of the transition).

Let us consider the transition of a system from a state 1 to a state 2 along the paths I and II (Fig. 7).

We shall split these paths into elements in which the system receives corresponding quantities of heat δQ at the temperature T . The total quantities of heat needed for the transition from 1 to 2 along these paths are equal respectively to

$$Q_I = \int_{(I)} \delta Q, \quad Q_{II} = \int_{(II)} \delta Q, \quad (3.AQ)$$

whereby according to the first law of thermodynamics we have, generally speaking,

$$Q_I \neq Q_{II}. \quad (3.AR)$$

However, if the quantity of heat δQ_i received by the system in a certain element of whatever path is divided by the temperature T_i at which this heat is communicated, and the sum (the integral) of these (reduced) quantities of heat along the entire first path and along the entire second path is found, then it is found (either experimentally or

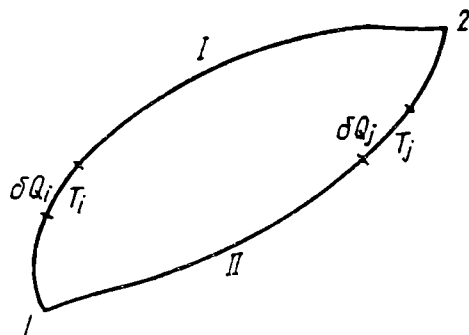


FIG. 7.

according to the second law of thermodynamics for quasi-static processes) that these sums (integrals) of reduced quantities of heat for the entire transition paths are equal:

$$\int_{(I)} \frac{\delta Q}{T} = \int_{(II)} \frac{\delta Q}{T}. \quad (3.38)$$

This indicates the existence of a certain single-valued parameter of state the variation of which is determined by this integral and is called entropy

$$S_2 - S_1 = \int \frac{\delta Q}{T}. \quad (3.4S)$$

The deep (statistical) meaning of entropy is revealed in statistical physics. From the molecular viewpoint the entropy of a system in a given state characterizes the probability of this state†

$$S = k \ln W, \quad (3.39)$$

where W is the probability of the state and k is Boltzmann's constant. The unilateral character of the variation of entropy in a closed system, which we shall discuss in the following section, is determined by the transition of a system from a less probable to a more probable state.

§ 16. The second law of thermodynamics for non-static processes

The existence, in an equilibrium system, of a new single-valued parameter of state—the entropy S —expresses the second law of thermodynamics for quasi-static processes.

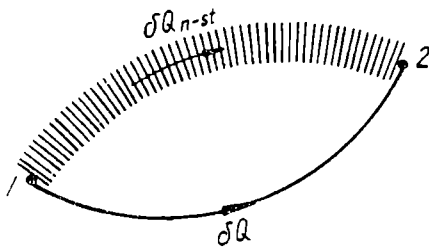


FIG. 8.

We shall formulate now the second law of thermodynamics as applied to non-static irreversible processes.

Let us consider (Fig. 8) two states of equilibrium 1 and 2, close to each other, of a certain system. Let us assume that, in a non-static transition from one state to the other,‡ a quantity of heat δQ_{n-st} is communi-

† See problem no. 42.

‡ In the diagram shown a non-static transition of the system is conventionally represented by a series of dashes, since such transitions cannot be represented on any diagram.

cated to the system from a thermostat and that the system accomplishes the work δW_{n-st} , so that, according to the first law of thermodynamics,

$$\delta Q_{n-st} = dU + \delta W_{n-st}. \quad (3.40)$$

If, however, the system passes quasi-statically from the state 1 to the state 2, then the quantity of heat obtained by it from the thermostat, will be, say, δQ and the work accomplished will be δW so that

$$\delta Q = dU + \delta W. \quad (3.41)$$

The first transition is irreversible, and therefore a return of the system to the initial state without compensation is impossible; the second transition is reversible and the system can return to the initial state without any variations whatsoever in the surrounding bodies. By subtracting the equation (3.41) from the equation (3.40) we shall obtain for the closed-cycle process

$$\delta Q_{n-st} - \delta Q = \delta W_{n-st} - \delta W. \quad (3.42)$$

This difference cannot be equal to zero, since in the opposite case this would mean that an irreversible process of transition of the system from one state to another could be reversed quasi-statically without variations in the surrounding bodies (by ceding to the thermostat the quantity of heat $\delta Q = \delta Q_{n-st}$ and carrying out the work $\delta W = \delta W_{n-st}$).

The difference (3.42) cannot be positive, since this would mean that, in the closed-cycle process resulting from the quasi-static return of the system, after an irreversible process to its initial state we would have accomplished the work $\delta W_{n-st} - \delta W > 0$ only at the expense of heat of the thermostat $\delta Q_{n-st} - \delta Q > 0$ without any compensation whatsoever.

The difference (3.42) can be negative since this corresponds to the fact that in returning the system, after an irreversible process, to the initial state in a quasi-static manner a portion of the heat, $\delta Q - \delta Q_{n-st} > 0$, is transferred to the thermostat at the expense of external work $\delta W - \delta W_{n-st} > 0$, which according to the second law of thermodynamics (its second part) is possible†

$$\delta Q_{n-st} - \delta Q = \delta W_{n-st} - \delta W < 0. \quad (3.AT)$$

† If the proposition of the impossibility of a perpetual motor of the second kind admitted of conversion, i.e. if work into heat also could not be converted fully without compensation, then the difference (3.42) could not be negative either. By satisfying the first condition (3.1) this would mean that the closed process shown in the figure is impossible. It is possible today to give an example of such a case (see §§ 45, 46).

Hence it follows that

$$\delta Q > \delta Q_{n-st}, \quad (3.43)$$

and

$$\delta W > \delta W_{n-st}. \quad (3.44)$$

The latter inequality has already been encountered by us in the particular case of work in the quasi-static and non-static expansion of a gas; here it has been established, on the basis of the second law of thermodynamics, for arbitrary non-static processes.

Since $\delta Q = TdS$ then from (3.43) we obtain

$$T dS > \delta Q_{n-st} \quad (3.AU)$$

and

$$dS > \frac{\delta Q_{n-st}}{T}, \quad (3.45)$$

and also

$$S_2 - S_1 > \int_1^2 \frac{\delta Q_{n-st}}{T}. \quad (3.46)$$

If the system passes from one state to another in a non-static adiabatic manner ($\delta Q_{n-st} = 0$) then from (3.45) and (3.46) we have

$$dS > 0 \quad \text{and} \quad S_2 - S_1 > 0, \quad (3.47)$$

i.e. the entropy increases in the process.†

This thesis of the increase of entropy in a closed system for non-static processes (*the law of the increase of entropy*) expresses the second law of thermodynamics for non-static processes. This gives us the possibility of describing the entropy as a measure of the irreversibility of processes in a closed system. In this consists the physical meaning of entropy, if we approach it from the viewpoint of the distinctive features of non-static processes.

† The fact that the entropy in adiabatic systems increases for non-static processes, and does not decrease, is connected with the condition determining the positiveness of absolute temperature. By taking the other additional condition, the one that leads to $T < 0$, we would have had from (3.45), for non-static processes in isolated (ordinary) systems, not a law of the increase but a law of the decrease of entropy.

Thus the law of the increase of entropy contains in itself not only an objective aspect (the unilaterality of natural processes) but also a subjective element, namely the sign of the absolute temperature, which only gives to the objective aspect a determined expression without altering its substance. It follows from this, among other things, that we cannot prove the positiveness of the absolute temperature by proceeding from the law of the increase of entropy, since the formulation of the second law of thermodynamics for irreversible processes in closed (ordinary) systems as the law of the increase of entropy already presumes that the absolute temperature is positive.

Since all natural, spontaneous, processes occur at a finite rate, i.e. they are non-static, then it follows that in these processes in closed systems the entropy always increases. Thus the second law of thermodynamics for non-static processes indicates the direction of natural processes: the latter in closed systems occur in the direction of increasing entropy.

From (3.46) we obtain for a closed-cycle process the inequality

$$\oint_{(\text{irr.})} \frac{\delta Q}{T} < 0, \quad (3.48)$$

which is called *Clausius' inequality*. Just as (3.46), this inequality expresses the second law of thermodynamics for *non-static* processes in non-isolated systems (in contrast to (3.47) which corresponds to adiabatic systems).

The fundamental equation of thermodynamics which expresses the first and the second law of thermodynamics can now be written in the form

$$T dS \geq dU + \sum A_i da_i, \quad (3.49)$$

in which the equality corresponds to quasi-static processes when $A_i = A_i(T, a_1, \dots, a_n)$ and coincides with the equation (3.32), while the inequality corresponds to non-equilibrium processes (in this case the generalized forces A_i are not functions of the temperature T and the external parameters a_i).

All further applications of thermodynamics are based on the equation (3.49). In this connexion the equation (3.49) with the equality sign determines the properties of equilibrium systems, while the expression with the inequality sign gives us the possibility of establishing equilibrium conditions of various thermodynamic systems.

Before we proceed to solve concrete physical problems on the basis of the fundamental equation of thermodynamics (3.49), we shall consider at first certain consequences of the second law of thermodynamics.

§ 17. Connexion between the thermic and caloric equations of state

The evaluation of many quantities requires, as we have seen, the knowledge of both the thermic equations and the caloric equations of state. These equations can be obtained independently of each other both experimentally and by methods of statistical physics. The second law of thermodynamics establishes a differential connexion between

these equations, which in certain cases makes the knowledge of the caloric equation of state unnecessary.

Let us establish this connexion. From the expression of the differential of entropy

$$dS = \frac{dU + \sum A_i da_i}{T} = \frac{\left(\frac{\partial U}{\partial T}\right)_{a_i} dT + \sum \left[\left(\frac{\partial U}{\partial a_i}\right)_{T, a_k} + A_i\right] da_i}{T} \quad (3.AV)$$

we have

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_{a_i} dT + \sum_i \left(\frac{\partial S}{\partial a_i}\right)_{T, a_k} da_i &= \\ &= \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{a_i} dT + \frac{1}{T} \sum_i \left[\left(\frac{\partial U}{\partial a_i}\right)_{T, a_k} + A_i\right] da_i \end{aligned} \quad (3.AW)$$

and therefore

$$\begin{aligned} \left(\frac{\partial S}{\partial T}\right)_{a_i} &= \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_{a_i}, & \left(\frac{\partial S}{\partial a_i}\right)_{T, a_k} &= \frac{1}{T} \left[\left(\frac{\partial U}{\partial a_i}\right)_{T, a_k} + A_i\right] \\ (i &= 1, 2, \dots, n), \end{aligned} \quad (3.AX)$$

but since

$$\frac{\partial^2 S}{\partial a_i \partial T} = \frac{\partial^2 S}{\partial T \partial a_i}, \quad (3.AY)$$

we obtain the following differential equation connecting thermic and caloric equations of state

$$T \left(\frac{\partial A_i}{\partial T}\right)_{a_i} = \left(\frac{\partial U}{\partial a_i}\right)_T + A_i. \quad (3.50)$$

If we substitute the value of the right-hand side of this equation in the expression of the differential of entropy, we shall obtain

$$dS = \frac{\left(\frac{\partial U}{\partial T}\right)_{a_i} dT + T \sum \left(\frac{\partial A_i}{\partial T}\right)_{a_i} da_i}{T}, \quad (3.AZ)$$

whence it can be seen that, owing to (3.50), the evaluation of entropy does not require the knowledge of the full caloric equation of state but only of the dependence of the internal energy on temperature. The equation (3.50) also enables us to find the caloric equation of state from the thermic equation of state and from only the T -dependence of U .

For a simple system subject to the action of a force of uniform pressure ($A = p$, $a = V$) the equation (3.50) has the form

$$T \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial U}{\partial V} \right)_T + p. \quad (3.51)$$

We shall apply (3.51) to the determination of the internal energy of an ideal gas and of a van der Waals' gas and to the evaluation of the difference of thermal capacities.

1. In the case of an ideal gas the thermic equation of state is Clapeyron's equation

$$pV = RT. \quad (3.BA)$$

From this equation we have $(\partial p / \partial T)_v = R/V$. By substituting in (3.51) we find Joule's law

$$\left(\frac{\partial U}{\partial V} \right)_T = 0, \quad (2.9)$$

which, as we have already indicated, leads to the caloric equation of state of an ideal gas

$$U = \int C_v dT \quad (3.BB)$$

and

$$U = C_v T + U_0 \quad (3.BC)$$

for a monatomic ideal gas.

2. For a real gas the thermic equation of which is van der Waals' equation

$$p = \frac{RT}{V-b} - \frac{a}{V^2}, \quad (3.BD)$$

we have

$$\left(\frac{\partial p}{\partial T} \right)_v = \frac{R}{V-b}. \quad (3.BE)$$

By substituting these data in (3.51) we shall obtain

$$\left(\frac{\partial U}{\partial V} \right)_T = \frac{a}{V^2} \quad (3.BF)$$

Thus

$$dU = \left(\frac{\partial U}{\partial T} \right)_v dT + \left(\frac{\partial U}{\partial V} \right)_T dV = C_v dT + \frac{a}{V^2} dV \quad (3.BG)$$

and

$$U = \int C_v dT - \frac{a}{V}. \quad (3.52)$$

Since C_V depends little on temperature, we can write (3.52) in the form

$$U = C_V T - \frac{a}{V} + U_0. \quad (3. \text{BH})$$

From the molecular viewpoint the first term in (3.52) represents the kinetic energy of the molecules of the gas, while the second term represents the potential energy of interaction of the molecules, which corresponds to the van-der-Waalsian forces of attraction.

3. The first law of thermodynamics gives for the difference of the thermal capacities $C_p - C_V$ the expression

$$C_p - C_V = \left[\left(\frac{\partial U}{\partial V} \right)_T + p \right] \left(\frac{\partial V}{\partial T} \right)_p. \quad (2.8)$$

To evaluate (2.8) we need to know both the thermic equation of state $p = p(T, V)$ and the caloric equation of state $U = U(T, V)$. The second law of thermodynamics by establishing a connexion between these equations of state, gives us the possibility of finding the difference $C_p - C_V$ from the knowledge of the thermic equation of state only.

In fact, by using (3.51)† we find

$$C_p - C_V = T \left(\frac{\partial p}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p. \quad (3.53)$$

The derivatives occurring here can be determined if we know merely the thermic equation of state $p = p(T, V)$ or else if we measure directly the coefficient of volume expansion

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p \quad (3. \text{BJ})$$

and the coefficient of thermal compression

$$\beta = - \frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_T. \quad (3. \text{BK})$$

From the identity (see problem no. 7)

$$\left(\frac{\partial V}{\partial T} \right)_p \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial T}{\partial p} \right)_V = -1 \quad (3. \text{BL})$$

† In the general case, according to (2.7) and (3.50), we have

$$C_A - C_a = T \left(\frac{\partial A}{\partial T} \right)_a \left(\frac{\partial a}{\partial T} \right)_A. \quad (3.53')$$

and the expression for α and β we find

$$\left(\frac{\partial p}{\partial T}\right)_V = -\left(\frac{\partial V}{\partial T}\right)_p \left(\frac{\partial p}{\partial V}\right)_T = \frac{\alpha}{\beta}. \quad (3.BM)$$

By substituting this derivative in (3.53) we find

$$C_p - C_V = \frac{V_0 T \alpha^2}{\beta}. \quad (3.54)$$

Since by the stability condition of an equilibrium state (see § 31) we always have $(\partial V/\partial p)_T < 0$ and, therefore, $\beta > 0$, then from (3.54) we obtain

$$C_p \geq C_V. \quad (3.BN)$$

The equality sign occurs for $\alpha = 0$ which is observed, for example, in water at 4°C when its density is a maximum and α changes its sign

$$\begin{aligned} \alpha < 0 & \quad \text{for} \quad 0 < t < 4^\circ\text{C}, \\ \alpha = 0 & \quad \text{for} \quad t = 4^\circ\text{C}, \\ \alpha > 0 & \quad \text{for} \quad t > 4^\circ\text{C}. \end{aligned} \quad (3.BO)$$

Such a behaviour of the coefficient of volume expansion in water leads to its anomalous property that, in the interval of temperatures $0 < t < 4^\circ\text{C}$, adiabatic compression does not give rise to heating, as with other liquids and all gases, but to cooling.†

§ 18. The efficiency of heat-engines. Carnot's cycle and Carnot's theorem. Types of heat-engines

1. As is well known, the second law of thermodynamics was historically established by proceeding from an analysis of the work of heat-engines.

In the first work on thermodynamics published by S. Carnot in 1824 the problem of the possible increase of the efficiency of heat-engines was formulated and solved. Carnot established two theorems on the efficiency of these machines, which together are equivalent to the second law of thermodynamics.

We shall prove these theorems by proceeding from the second law.

The efficiency η of a heat-engine is the ratio of the work produced by the machine during a cycle to the quantity of heat Q_1 received by the machine during this cycle:

$$\eta = \frac{W}{Q_1}. \quad (3.BP)$$

† See problem no 45.

According to the first law $W = Q_1 - Q_2$ where Q_2 is the absolute value of the quantity of heat rejected by the working body during a cycle, and therefore

$$\eta = \frac{Q_1 - Q_2}{Q_1}. \quad (3.BQ)$$

We shall evaluate the efficiency of Carnot's cycle which consists of two isothermal and two adiabatic processes.†

On the $S-T$ diagram this cycle is represented in the form shown in Fig. 9. Along the isothermal 1-2 the heat Q_1 is taken from the heater, and along the isothermal 3-4 the heat Q_2 is ceded to the cooler. According to the second law of thermodynamics for quasi-static processes in the form of Clausius' equality (3.8), we have for one cycle

$$\oint \frac{\delta Q}{T} = 0, \quad (3.BR)$$

or

$$\int_1^2 \frac{\delta Q}{T} + \int_2^3 \frac{\delta Q}{T} + \int_3^4 \frac{\delta Q}{T} + \int_4^1 \frac{\delta Q}{T} = 0, \quad (3.BS)$$

or

$$\Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0. \quad (3.BT)$$

But

$$\Delta S_{12} = \int_1^2 \frac{\delta Q}{T} = \frac{Q_1}{T_1}, \quad \Delta S_{23} = 0, \quad \Delta S_{34} = \int_3^4 \frac{\delta Q}{T} = -\frac{Q_2}{T_2}, \quad \Delta S_{41} = 0,$$

and therefore

$$\frac{Q_1}{T_1} - \frac{Q_2}{T_2} = 0, \quad (3.BV)$$

whence

$$\frac{Q_2}{Q_1} = \frac{T_2}{T_1}, \quad \frac{Q_2 - Q_1}{Q_1} = \frac{T_2 - T_1}{T_1}, \quad (3.BW)$$

and eventually the efficiency of Carnot's cycle is equal to

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}. \quad (3.55)$$

It can be seen from this that *the efficiency of Carnot's cycle does not depend on the working substance but is determined only by the temperature of the heater and the temperature of the cooler (Carnot's first theorem).*

† In Carnot's time this cycle was a good scheme of operation of steam engines then widely employed.

It also follows from (3.55) that the effect of a variation of the temperatures T_1 and T_2 on the value of the efficiency of Carnot's cycle is different.

(3.BX)

$$\frac{\partial \eta}{\partial T_1} = \frac{T_2}{T_1^2}, \quad \frac{\partial \eta}{\partial T_2} = -\frac{1}{T_1} = -\frac{T_1}{T_1^2},$$

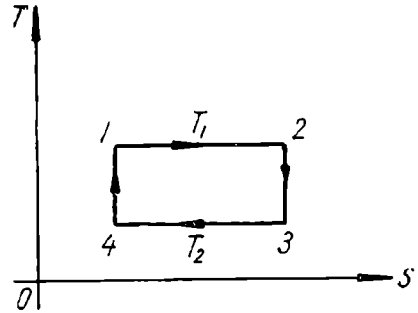


FIG. 9.

and since $T_1 > T_2$ then $|\partial \eta / \partial T_1| < |\partial \eta / \partial T_2|$. Thus a variation of the temperature of the heater affects the efficiency of Carnot's cycle to a smaller extent than does a variation of the temperature of the cooler.

Carnot's theorem shows the way to obtaining higher efficiencies in heat-engines. It has played a leading role in the development of heat engineering. Though no heat-engine is used in modern engineering works according to Carnot's cycle, its importance consists in that this cycle has the greatest efficiency in comparison with cycles working within the same temperature limits (see problem no. 56) and is a measure of the limit of efficiency of all other cycles.†

If a machine works along an irreversible cycle and receives during the cycle the same quantity of heat Q_1 as in a reversible cycle then, since by (3.44) the work W_{n-st} during an irreversible cycle is less than the work along the same reversible cycle W , the efficiency of an irreversible machine $\eta_{irr} = W_{n-st}/Q_1$ is smaller than the efficiency of a reversible machine $\eta = W/Q_1$ (Carnot's second theorem):

$$\eta_{irr} < \eta_{rev}. \quad (3.56)$$

2. According to the use for which they are intended, heat machines are divided into three basic types: heat-engines, heat pumps (heating machines) and refrigerating machines.

Heat-engines, which we have discussed above, transform heat into work, heat pumps use expended work and the heat extracted at the same time from the medium (at lower temperature) for heating a body of higher temperature, and refrigerating machines by the expenditure of work remove heat from the body to be cooled and transmit it to the surrounding medium. When these machines operate continuously the working substance in them accomplishes a closed-cycle process: in

† However, for given limit values of pressure or volume Carnot's cycle is not the most convenient. This is why it is not used in modern heat-engines.

heat-engines a direct closed-cycle process, and in the heat pump and in refrigerators the reverse closed-cycle process.

During a cycle, by the first law of thermodynamics $\oint \delta Q$ is equal to W or $Q_1 = Q_2 + W$, where Q_1 is the quantity of heat taken from (or, in the reverse cycle, communicated to) the high-temperature body, and Q_2 is the quantity of heat transmitted to (or taken from) the body (or the surrounding medium) of low temperature. For a heat-engine (the direct cycle) we always have, by the second law, $Q_1 > W$, and for a heat pump and refrigerating machine (the reverse cycle) $W \leq Q_1$ (the equality occurs for $Q_2 = 0$ which, in contrast to the direct cycle, is always possible in the reverse cycle; only the expended work is converted in this case into heat).

The intended use of a heat-engine is characterized by its efficiency

$$\eta = \frac{W}{Q_1}, \quad (3.BY)$$

which, according to what has been expounded above is always less than unity.

The intended use of a heat pump is characterized by the coefficient of performance

$$\varphi = \frac{Q_1}{W}, \quad (3.BZ)$$

which is always greater than unity (for $Q_2 = 0$, $\varphi = 1$, but in this case the high-temperature body receives heat only at the expense of work and the machine is no longer a heat pump in the normal sense).

The purpose of a refrigerating machine is characterized by the refrigerating coefficient of performance

$$\psi = \frac{Q_2}{W}, \quad (3.CA)$$

i.e. by the ratio of the heat removed from the cold body to the expended work. It can easily be seen that ψ can be either larger or smaller than unity and can also be equal to zero. In fact, from $W = Q_1 - Q_2$ we obtain $Q_2/W = Q_1/W - 1$, or $\psi = \varphi - 1$. But $\varphi = Q_1/W > 1$ and therefore $\psi = Q_2/W$ can be both greater than 1 (when $\varphi > 2$) and smaller than 1 (when $1 < \varphi < 2$); for $\varphi = 1$ (i.e. for $Q_2 = 0$) $\psi = 0$.

The combination of a heat-engine working over a temperature interval with a heat pump working over another temperature interval is a thermotransformer, i.e. a device by means of which a determined quantity of heat obtained from a body of given temperature is trans-

formed to another quantity of heat of a different temperature. According to their operation, thermotransformers are divided into step-up, step-down and mixed type.†

§ 19. Spontaneous flow of heat

The second law of thermodynamics for non-static processes indicates a determined direction of natural processes. This can be seen especially well in the example of the spontaneous flow of heat when two bodies with different temperatures are in thermal contact.

Let us bring into contact two bodies with temperatures T_1 and T_2 . When equilibrium has been established the temperatures will have been equalized; suppose that in this connection a quantity of heat $\delta Q > 0$ is transmitted during the time dt from the body of temperature T_1 to the body of temperature T_2 . By the second law, the entropy of this system of bodies must increase in the process, and therefore

$$dS = dS_1 + dS_2 = -\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) > 0, \quad (3.57)$$

whence $T_1 > T_2$, i.e. heat flows spontaneously from the body with higher temperature to the body with lower temperature.

The well-determined direction, the unilateralness of the flow of heat for the thermal contact of two bodies having different temperatures is an objective law of nature. However, the concrete expression of this law depends on the definition of the concept of greater or smaller temperature, or, which is the same, on the choice of the sign of the absolute temperature (for ordinary systems).

If we assume a negative absolute temperature (this would mean that, in communicating heat to an ordinary body for constant external parameters, the temperature of the body decreases) then the second law for non-static processes would consist in the statement of the decay of entropy in closed systems for adiabatic processes. Then the expression (3.57) would be written in the form

$$dS = \delta Q \left(\frac{1}{T_2} - \frac{1}{T_1} \right) < 0, \quad (3.CB)$$

whence $T_1 < T_2$, i.e. heat flows spontaneously from a body with lower temperature to a body with higher temperature.

Having assumed a positive absolute temperature we arrive at an expression of the unilateral character of the spontaneous flow of heat in the thermal contact of two bodies in the form $T_1 > T_2$.

† See V. S. Martynovskii, *Teplovyye nasosy* (Heat Pumps), Gosenergoizdat, 1953.

The unilateral character of heat transmission can serve as the basis for defining the concept of larger or smaller temperature. Generally speaking, this concept can be defined both within the limits of quasi-static processes (in communicating heat to a body its temperature *increases*) and by an analysis of non-static processes (if of two bodies A and B in thermal contact heat flows A to B , then the temperature of the body A is *larger* than the temperature of body B). The second law shows that the two definitions are not independent of each other so that the definitions given in the text do not contradict each other (see § 31).

In the scientific and pedagogical literature the statement is often encountered that the law of the increase of entropy and the fact of the existence of entropy are independent theses, since the latter is perfectly compatible with the opposite thesis “the law of decreasing entropy” or any other. However we must observe the following. Just as we have seen, if we take the absolute temperature (for ordinary systems) to be positive, then *only* the law of the increase of entropy is compatible with the fact of the existence of entropy and the law of the decrease of entropy is incompatible with this fact; if, however, a negative absolute temperature is taken the contrary will be true. On the other hand, the result that the absolute temperature cannot vary its sign (in quasi-static processes) is a consequence of the fact of the existence of entropy in every equilibrium system, and the choice of this sign depends on the definition of the concept of higher or lower temperature.

The second law of thermodynamics effectively consists of two independent theses which are expressed either in the form

$$Q \underset{\rightarrow}{>} W \quad \text{and} \quad W \underset{\rightarrow}{=} Q, \quad (3. CC)$$

or, in the language of entropy, in the fact of the existence of entropy and its unilateral variation in non-static processes in adiabatic closed systems.

§ 20. Limits of applicability of the second law. The “theory” of the thermal death of the universe

The second law of thermodynamics is an expression of the natural features proper of phenomena connected with thermal motion. It establishes a difference of principle of the microphysical form of transmission of energy, heat, from the macrophysical form which is connected with a variation of external parameters, work. This difference which leads to the existence and to the increase of entropy is valid both in large

and in small bodies. However, in the case of systems the dimensions of which are comparable with the dimensions of molecules, the difference between the concept of heat and work vanishes, and therefore the thermodynamic parameters, entropy, temperature etc., have no meaning for such microsystems.†

This leads to the statement that the second law of thermodynamics is inapplicable to microsystems. The latter does not mean that in such systems the second law is violated—we cannot implement a perpetual motor of the second kind whatever the systems we use‡—it only means that to speak of a perpetual motor of the second kind as a device capable of converting heat into work without compensation would be without a meaning when applied to microsystems, since for them the distinction between heat and work does not exist.

Thus a lower boundary of applicability exists for the second law and therefore for all thermodynamics: the second law is inapplicable to microsystems.

An upper boundary of applicability of thermodynamics can also be shown. The initial thesis of thermodynamics of the thermal equilibrium, of the steady transition of an isolated system to an equilibrium state and the self-indestructibility of this state, and the law of the increase of entropy in such systems are the result of generalizations of experimental data in systems of finite dimensions. The uncritical extension of these laws to systems of infinite dimensions, without an analysis of the profound qualitative variations that can be involved in such a transition from finite to infinite systems, can lead and has actually led certain scientists to anti-scientific conclusions on the so-called thermal death of the universe.

The “theory” of the thermal death of the universe was explicitly formulated about one hundred years ago by Clausius†† who, by extending the law of thermodynamics

† Therefore such systems are not thermodynamic systems.

‡ It might appear at first sight that the presence of fluctuations gives us in principle the possibility of constructing a perpetual motor of the second kind. However, this is not so. Let us consider, for example the fluctuation of density in a gas. It might appear possible to “catch” the pressure differences arising by means of special valves and apparatus capable of dealing with single molecules (such devices were called by Maxwell, demons (consciousness, intelligence)) and to use them for accomplishing work or for separating a mixture of gases. This is however, impossible not only practically but also theoretically. All our apparatus, valves etc. themselves consist of molecules and themselves exhibit oscillations about the position of equilibrium, these being completely independent of the oscillations of gas density. The desired result could be obtained at a certain instant of time, but would be compensated at the next instant by the oscillations of the apparatus and the gas.

†† Since then, this pseudo-scientific theory has obtained fairly wide acceptance in bourgeois scientific circles. Anti-scientific fabrications on the “thermal death” of the universe are being diffused also in our times by certain bourgeois scientists. Thus, for example, in Jeans’ *The Universe Around Us* (1930, p. 328) we read: “The universe cannot exist for ever; sooner or later a time must come when its last erg of energy will reach the highest step on the ladder of decreasing usefulness, and, at this instant, the active life of the universe must cease.” Eddington in *The Nature of the Physical World* (1935, p. 90) wrote: “The entire universe will reach thermal equilibrium in the future at a time that is not indefinitely remote. There exists a trend of thought that finds the idea of the wear of the world frankly repellent. Various rejuvenation theories are favoured by this school. But I confess that I have personally no great desire that the final stopping of the universe be averted. . . I would feel more gratified if the universe accomplished some great scheme of evolution and, having accomplished all that could be accomplished, fell back to chaotic immutability, than if its purpose were debased by unwearying repetition”.

to the entire infinite universe wrote: "The energy of the world remains constant, the entropy of the world tends to a maximum". This means that the universe will sooner or later arrive at a state of thermodynamic equilibrium; then all processes will cease and settle down in a state of "thermal death": the temperature at all places of the universe will be one and the same, all other intensive factors will be equalized and there will be no more causes capable of giving rise to any process whatsoever.

This "theory" of the thermal death leads directly to religious superstition—to the existence of God. In fact, since according to Clausius the universe moves continuously towards thermodynamic equilibrium, while it is not in an equilibrium state at the present moment, then it follows that either the universe has not always existed and has been somehow created, or some sort of external force has at some time removed it from its equilibrium state and we are now living the epoch of the returning of the universe to a state of equilibrium. This means that God must exist.†

The reactionary views of Clausius have been subject to Engels' crushing criticism. From the positions of dialectic materialism Engels proved the complete inconsistency of the "theory" of the thermal death. In his *Dialectics of Nature* he wrote: "In whatever form the *second thesis of Clausius* etc. is put forward, in any case according to him energy is lost qualitatively if not quantitatively. *Entropy cannot disappear by natural means but instead can be created.* The world at the beginning must have been wound up and then it will go until it reaches a state of equilibrium, and only a miracle can move it away from this state and start it back into motion. The energy expended to wind up the clock has disappeared, at least qualitatively, and can only be restored by means of a *stimulus from without.* Thus a stimulus from without was also needed at the beginning; thus the quantity of motion or energy available in the universe is not always the same; thus energy must have been created; thus energy can be created; thus energy can be destroyed" (F. Engels, *The Dialectics of Nature*, Gospolitizdat, 1952, p. 229).

Engels shows in this manner that the "theory" of the thermal death of the universe contradicts the theory of conservation and transformation of energy, since this law, as we have already indicated, affirms not only the quantitative indestructibility of motion of matter but also its never-exhausted ability for qualitative transformations of various forms of motion into one another.

"The indestructibility of motion—wrote Engels—is to be understood not only in a quantitative but also in a qualitative sense. Matter, the purely mechanical displacement of which does contain in itself the possibility of transformation under favourable conditions into heat, electricity, chemical action, life, but which is not in a state of generating by itself these conditions, *such matter would suffer a certain deterioration in its motion.* Motion that had lost its capacity for transformation into different forms peculiar to it, though it still possesses *dynamis* (possibility) it no longer possesses *energeia* (efficacy) and thus is partially destroyed. But such motion and such matter are unthinkable" (*ibid.*, p. 17).

Engels established the falsity of the conception of the possibility itself of thermal equilibrium in a universe infinite in space and time, for in moving matter itself there lies the cause of its motion. He wrote: "... matter in all its transformations always remains one and the same, none of its attributes can ever be exhausted and therefore by

† In 1952 in his address to a session of the "Pontifical Academy of Sciences" the Pope Pius XII said: "The law of entropy discovered by Rudolph Clausius has given us the certainty that spontaneous natural phenomena are always connected with a certain loss of the free energy capable of utilization, whence it follows that in a closed material system those processes at the macroscopic scale will in the end at some time cease. This sad necessity... is an eloquent evidence of the existence of a Necessary Being".

the same iron necessity by which some day it will destroy on Earth its highest flower, intelligence, it must again generate it somewhere in another place at another time (*ibid.*, p. 19).

Leading scientists of the last century have also come forward against Clausius' conception of the thermal death of the universe.

Of great progressive value are, in this connexion, the works, first of all, of the leading physicist-materialist Boltzmann and the works of the well-known Polish physicist-materialist Smoluchowski.

To counteract the "theory" of the thermal death of the universe Boltzmann advanced the so-called "fluctuation hypothesis". Boltzmann was the first to establish the statistical nature of the second law of thermodynamics. According to Boltzmann, a state of thermodynamic equilibrium is only one that occurs most often, a most probable state; in an equilibrium system there can always spontaneously arise arbitrarily large fluctuations.

By extending these deductions to the whole universe, Boltzmann arrives at the conclusion that the universe is found, generally speaking, in a state of thermodynamic equilibrium; in it, however, there inevitably arise arbitrarily large fluctuations. Such an enormous fluctuation is the part of the universe in which we are found. Each fluctuation must vanish but equally inevitably there will arise fluctuations of a similar kind in other places of the universe. Thus, according to Boltzmann, some worlds perish and others come into being.

In his *Lectures on the Theory of Gases* (§ 90) Boltzmann wrote† "We can think of the universe as a mechanical system consisting of an enormous number of component parts and with an enormous duration of existence, so that the dimensions of our system of fixed stars are negligible in comparison with the extension of the universe and the duration of its existence. Then in the universe which, in general, is found everywhere in a state of thermal equilibrium, i.e. death, here and there comparatively small regions of the extension of our stellar system must exist (we shall call them solitary worlds), that in the course of a comparatively brief time era deviate considerably from thermal equilibrium, there being equally parts in which the probability of state increases and parts in which it decreases. Therefore, for the universe, the two directions of time are indistinguishable, just as in space there exist no up and down. But, just as at a determined point of the Earth's surface the direction towards the centre of the Earth is defined as the down direction, living substance that is found at a determined phase of time on such a solitary world will determine the direction of time towards less probable states rather than the opposite direction (the first as the past, the origin, and the second as the future, the end), and, in accordance with such designation, the small "beginning" regions, isolated from the universe, will always be found in a small probability state. This method seems to me the only method by which we can conceive the second law, the thermal death of each solitary world, without a unilateral variation of the whole universe from a determined origin to an ultimate final state."

Smoluchowski, who had brilliantly proved the existence of fluctuations, was a partisan of Boltzmann's view. In one of his declarations he said: "Clausius maintained, on the basis of empirical thermodynamics, that the entropy of the universe continually increases, and that, therefore, the universe must pass, in time, to a stage of numbness, the notorious Waermetod, in which all potential energy will be converted into heat and all differences in temperature will be equalized. The kinetic theory, on the contrary, maintains that after a stage of numbness new life will again arise, since all states return with time in perpetual rotation."

Boltzmann, Smoluchowski and, in our time, many others consider that the fallacy of the deduction of the thermal death of the universe lies in conceiving the laws of

† L. Boltzmann, *Lektsii po teorii gazov* (transl.), Gostekhizdat (1956).

thermodynamics as absolute laws, i.e. in neglecting the statistical nature of the second law, since the fluctuation hypothesis supported by them rejects the "theory" of the thermal death on the basis of the statistical nature of the second law. As a matter of fact the "theory" of the thermal death of the universe has been falsely developed not as a consequence of ignoring the statistical nature of the second law but, on the contrary, owing to the inapplicability of the second law to infinite systems as a consequence of its statistical nature. This has been shown recently by I. R. Plotkin who in his paper "On the increase of entropy in an infinite universe" (*Zh. eksp. teor. fiz.* 20, 1051 (1950)) has established that in an infinite universe there exist no more probable states (the concept of thermodynamic equilibrium as the most probable state has, therefore, no meaning when applied to the universe) and therefore the law of the increase of entropy, which is valid in finite isolated systems, is ineffective in the whole universe or in an infinite part of it (see problem no. 64). In passing from finite to infinite systems a qualitative saltus occurs in the temporal evolution of such systems. This establishes an upper bound of applicability of the second law and reveals the fallacy of the formulation itself of the question of the thermal death of the universe.

The metaphysical character of Boltzmann's hypothesis can also be seen from the fact that, according to Boltzmann, the development of the World has the character of thermal fluctuations on a general background of "thermal death" and not as a motion along an ascending line, not as the transition from an old qualitative state to a new qualitative state, not as a development from simple to complex, from lower to higher, as is considered by dialectic materialism.

Boltzmann's deduction according to which a state of thermodynamic equilibrium prevails in the universe, is contradicted more and more by the growing experimental data of astronomy. At the same time this astronomic material confirms the views of dialectic materialism on the development in nature. The recent observations and discoveries of astrophysicists on the arising and development of stellar associations show that matter never exhibits an exhaustion of its capacity for energy concentration and for transformation of forms of motion into one another. At the same time they establish that the process of formation of stars from dispersed matter obeys determined laws, goes through determined stages and in no case can be reduced to random fluctuations of the distribution of energy in the universe.

PROBLEMS

28. Is a process possible, in which heat taken from a thermal source is entirely converted into work?

29. Attempts were repeatedly made in the last century to find such processes as would prove a contradiction to the second law. A more accurate analysis of such processes has shown each time that their contradiction to the second law is only apparent. W. Wien's light-valve† paradox (1900) belongs to this group.

Between two bodies of equal temperature there is situated a light valve (Fig. 10). Light from the body 1 is incident on the prism I. One half of the incident energy J , i.e. $J/2$, is transmitted through the prism I, then through the prism II and is absorbed

† A light valve is a device as follows: two Nicol prisms are situated on the path of a ray of light in such a manner that their principal planes are rotated by 45° with respect to each other; between them there is found a layer of a substance in which a rotation of the plane of polarization is caused by a static magnetic field directed along the ray, for example from the first Nicol prism to the second (Faraday's phenomenon). In contrast to a natural rotation of the plane of polarization (without a magnetic field, for example a sugar solution) the direction of rotation of the plane of polarization is

by the body 2, while the other half, after total internal reflection in the prism I is returned by the mirror S_1 to the body 1. On the other hand, the light sent by the body 2 is not transmitted by the light valve. Half of the energy J radiated by this body, equal to $J/2$, after total internal reflection in the prism II, will return, by reflection

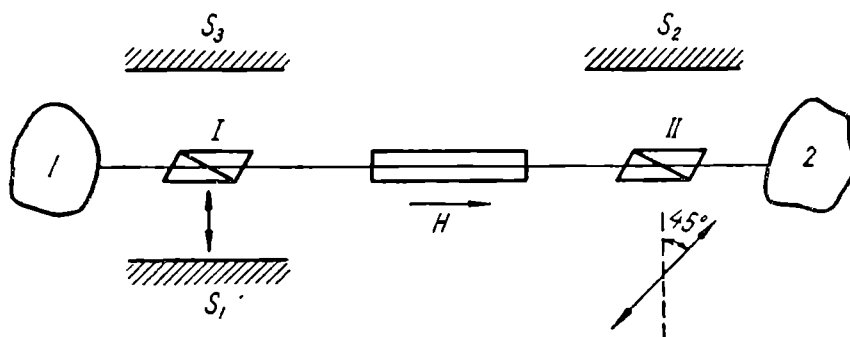


FIG. 10.

from the mirror S_2 to the body 2. The second half of the energy, on passing through the prism II, will traverse the rotating medium undergoing a rotation of the plane of polarization by 45° , will not be transmitted through the prism I but, by total reflection in it, will be reflected back by the mirror S_3 , and, after total internal reflection in the prism I will return to the body 2. Thus the body 1 receives the energy $J/2$ and the body 2 the energy $3J/2$ and will be heated in contradiction to the second law of thermodynamics. Wien reckoned that compensation for heating the body 2 will be obtained on account of some unknown processes in the magneto-rotating substance. Rayleigh pointed out an elementary error in the above reasoning by Wien. In what does this error consist?

30. On a hot sand-bath there is placed a high hard-glass test tube on the bottom of which a layer of aniline is poured and above it a sufficiently large quantity of water. After a certain time a drop of aniline rises to the surface of the water by accomplishing work against the gravitational forces and then falls again to the bottom. This process will be repeated as long as the bath is heated. How can we explain such a motion of the drop? Does it not contradict the second law on the impossibility of periodically accomplishing work at the expense of heat from a single thermal source?

31. A beautiful transparent illustration of the second law of thermodynamics is provided by the Chinese "duckling" toy, which should become a standard device for physical demonstration in every physical laboratory. The "duckling" (Fig. 11) is a hermetically-

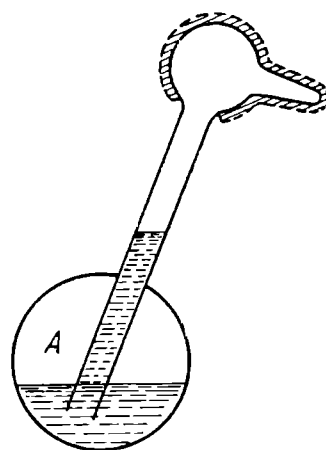


FIG. 11.

not determined by the direction of the ray but by the direction of the magnetic field. Therefore if the intensity of the magnetic field has been so chosen that in the propagation of light from the prism I to the prism II the plane of polarization is rotated by 45° and light passes through the prism II, then in a ray of opposite direction, in the propagation of light from prism II to prism I, the plane of polarization will be rotated by 45° in the same direction as in the first case and light does not pass through the prism I.

sealed shaped ampule of glass on a metal base. The ampule is filled with a volatile liquid. In equilibrium the stem of the duckling is inclined by several degrees with respect to the vertical. The head and the beak are covered with a thin layer of cotton wool. If the head is somewhat moistened, for example, by lowering the beak in a little glass containing water, the duckling itself will after this continually "drink" water from the little glass. Explain such a behaviour of the duckling.

32. The process of diffusion of different gases is irreversible. How can we accomplish the mixing of gases reversibly?

33. Show that entropy increases in the following processes:

(a) Hot water cedes heat to an equal mass of cold water and their temperatures are equalized.

(b) Two equal vessels adiabatically isolated from the surrounding medium and containing equal masses of ideal gases at different pressures are connected by a tube with a stop-cock. The stop-cock is opened and the states of the gas in both vessels become the same.

34. The holonomicity of the element of heat δQ occurs only for thermally homogeneous systems. Show that a thermally non-homogeneous system will be non-holonomic.

35. The content of the second law of thermodynamics for quasi-static processes is, according to Carathéodory, the holonomicity of the element of heat δQ . In his book "Thermodynamics" Planck presents this remarkable fact as something trivial, expressing no special properties of bodies: by the example of an ideal gas he evaluates directly the expression $\delta Q/T$ and satisfies himself that it is a total differential, while he reckons it possible to prove that this expression will be a total differential also for any other system by considering the complex system consisting of an ideal gas G and the given system S . He lets this complex system $G + S$ accomplish a closed-cycle process in which no heat is received from without. Then both G and S must separately accomplish a closed-cycle process in which connexion we have evidently

$$\oint_G \frac{\delta Q}{T} + \oint_S \frac{\delta Q}{T} = 0. \quad (3. CD)$$

Hence $\oint_G \frac{\delta Q}{T} = 0$ since by the previous calculation $\oint_S \frac{\delta Q}{T} = 0$. Planck considers that by this means he has proved that $\delta Q/T$ is a total differential for every system.

T. A. Afanas'yeva-Ehrenfest has pointed out that an error has escaped Planck's attention in the above proof. In what does this error consist?

36. Show that: (a) adiabatics cannot intersect each other, (b) an isothermal cannot intersect twice a given adiabatic.

37. Show that the Pfaffian forms in two variables are always holonomic.

38. Show that in the case of a non-holonomic Pfaffian form any two points x_1^0, x_2^0, x_3^0 and x_1^1, x_2^1, x_3^1 can always be connected by an adiabatic.

39. By Gibbs' theorem the entropy of a mixture of two ideal gases filling the volume V is equal to the sum of the entropies of the two gases separately, evaluated on the assumption that each of them occupies the whole volume V . Show that this theorem is not valid in the case of identical gases and explain Gibbs' paradox.

40. 30 litres of NO diffuse into 30 litres of SO_2 at the constant common pressure of 2 atm at a temperature of 0°C . Evaluate the increase of entropy.

41. The entropy of ν moles of an ideal gas, which occupy at the temperature T the volume νV (V is the volume of one mole), is equal to $S_\nu = \nu C_V \ln T + \nu R \ln (\nu V) + b_\nu$. How must the constant b_ν depend on ν (and therefore on the number of particles $N = \nu N_0$, where N_0 is Avogadro's number) in order that the additive property of entropy be satisfied?

42. Assuming that between the entropy S and the probability W of a state of a system there exists a certain functional relationship (Boltzmann's principle) and using the general properties of entropy and probability, establish Boltzmann's relation $S = k \ln W$.

43. Two bodies at temperatures of 27°C and 28°C respectively are brought into contact. Over a certain period of time a quantity of heat equal to 1 erg will flow from the hotter to the colder body. Determine by how many times the probability of state of the given bodies will have varied as a consequence of this flow of heat. To what is equal the probability of the reverse flow? How will the result vary for the flow of a quantity of heat equal to 1.2×10^{-6} erg?

44. A system passes reversibly from a state 1 to a state 2 (Fig. 12) by receiving from a thermostat a quantity of heat δQ and accomplishing work δW , and is returned from the state 2 to the state 1 irreversibly by receiving from the thermostat a quantity of heat δQ_{n-st} and accomplishing work δW_{n-st} . Show that in this case the

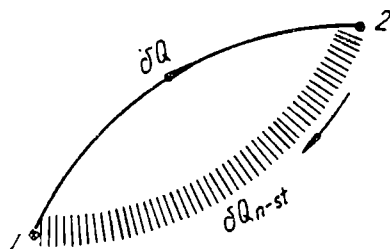


FIG. 12.

work of the system for the non-static transition is always less than the work of the system for the quasi-static transition. Observe that in the presence of non-static processes a closed-cycle process is possible with non-zero work with a single thermostat.

45. The coefficient of volume expansion, α , of water at 4°C changes its sign and for $0^\circ < t < 4^\circ$ it will be a negative quantity. Show that, over this interval of temperatures, water is cooled by adiabatic compression and not heated like other liquids and all gases.

46. Show that the temperature $t = 4^\circ\text{C}$ cannot be reached in water by cooling (heating) it by means of an adiabatic expansion.

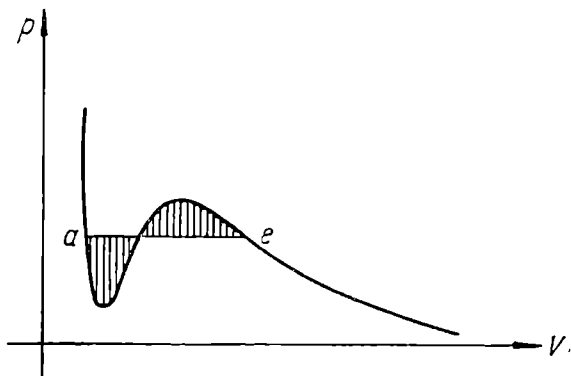


FIG. 13.

establish Maxwell's rule: on the V, p diagram the areas formed by the intersection of van der Waals' isothermal with the experimental isothermal-isobaric ae (Fig. 13), which corresponds to liquid-vapour equilibrium, are equal.

49. Evaluate the entropy of a van der Waals' gas and find the equation of its adiabatic.

50. Evaluate the difference $C_p - C_v$ for a van der Waals' gas.

51. By using the differential equation (3.50) which connects the thermic and caloric equations of state show that the thermic equation of state of an ideal paramagnet has the form $M = f(H/T)$.

47. Let us consider Carnot's cycle with water as the working fluid. The temperatures of the cooler and the heater are equal respectively to 2° and 6°C . At 6°C water is expanded and at 2°C it is isothermally compressed. Owing to the anomalous behaviour of water for $t < 4^\circ\text{C}$, heat will be abstracted at both temperatures and will be completely converted into work, which is found in contradiction with the second law. How can we resolve this contradiction?

48. By using the fundamental equation of thermodynamics, es-

52. Show that for paramagnets that satisfy Curie's law $\chi = C/T$ (χ is the paramagnetic susceptibility and C is Curie's constant) the internal energy does not depend on the magnetization M (or the magnetic field H).

53. Evaluate the difference $C_E - C_A$ between the thermal capacities at constant tension and at constant deformation for a solid elastic rod.

54. Evaluate the difference $C_E - C_D$ between the thermal capacities of a dielectric at constant field intensity E and constant induction D .

55. Show that for substances whose thermic equation is such that pressure is a linear function of the temperature T , the thermal capacity C_V will not depend on volume.

56. Show that Carnot's cycle has the largest efficiency in comparison with all other cycles within the same temperature limits.

57. Evaluate the efficiency of an air-engine that works according to Stirling's cycle consisting of two isothermals $T = T_1$ and $T = T_2$ and two isochores $V = V_1$ and $V = V_2$, and compare it with the efficiency of a machine working according to Carnot's cycle with the same temperature limits T_1 and T_2 .

58. Find the efficiency of an internal combustion engine working according to Otto's cycle, for which the ignition of the fuel occurs at a constant volume and the indicator diagram of which is shown in Fig. 14. The parameter of the cycle is the compression ratio $\epsilon = V_1/V_2$.

59. Find the efficiency of an internal combustion engine that works according to Diesel's cycle the diagram of which is shown in Fig. 15. The parameters of the cycle are the compression ratio $\epsilon = V_1/V_2$ and $\rho = V_3/V_2$, the isobaric expansion ratio.

60. Determine the value of the coefficient of performance φ of a heat pump and the value of the refrigerating coefficient ψ of performance

of a refrigerating machine when the closed-cycle process in both machines is Carnot's reversed cycle with temperature limits T_1 and T_2 ($T_1 > T_2$). Show that variations of the temperatures T_1 and T_2 affect φ and ψ in different ways.

61. In a step-down thermotransformer the heat-engine removes the heat Q_1 from a body at high temperature T_1 , cedes a portion of the heat, Q_2 , to a body with a lower temperature T_2 ($T_2 < T_1$) and accomplishes the work W which is used by the heat pump for extracting the heat Q_0 from the medium with a still lower temperature T_0 ($T_0 < T_2$) and for transmitting to the body with temperature T_2 a quantity of heat Q'_2 . Altogether this equipment accomplishes no work but, at the expense of the heat Q_1 of the body of high temperature T_1 , the body with lower temperature T_2 receives the heat $Q = Q_2 + Q'_2$. The transformation coefficient of a step-down thermotransformer n is defined as the ratio of the quantity of heat Q received by the body of lower temperature T_2 to the expended heat Q_1 of the body of high temperature T_1 ; $n = Q/Q_1$. Express n in terms of the efficiency η of the heat-engine and of the coefficient of performance of the heat pump as well as in terms of the temperatures T_1 , T_2 and T_0 , by assuming that both machines work according to suitable Carnot cycles (direct and reverse).

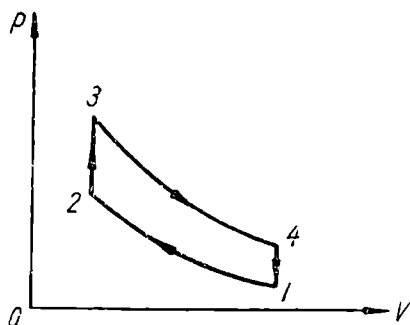


FIG. 14.

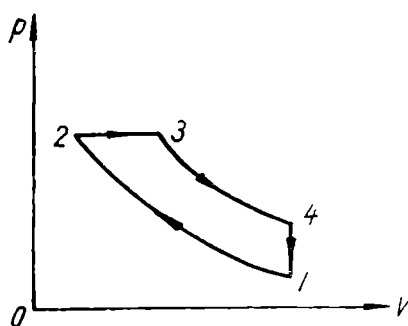


FIG. 15.

62. In a step-up thermotransformer the heat-engine removes the heat Q_2 from the body with lower temperature T_2 , cedes the heat Q_0 to the medium with still lower temperature T_0 ($T_0 < T_2$) and produces work W that is used by the heat pump to extract the heat Q'_2 from the body with temperature T_2 and to transmit the heat Q_1 to the body with high temperature T_1 ($T_1 > T_2$). In the end, such an aggregate of heat-engine and heat pump leads to the transfer of heat Q_1 from the cold body (T_2) to the hot body (T_1). The transformation coefficient of the step-up thermotransformer n_+ is defined as the ratio of the quantity of heat Q_1 received by the body at high temperature T_1 to the quantity of heat $Q = Q_2 + Q'_2$ extracted from the body of lower temperature T_2 : $n_+ = Q_1/Q$. Express n_+ in terms of η of the heat-engine and of φ of the heat pump as well as of the temperatures T_1 , T_2 and T_0 , by assuming that both heat machines work according to suitable Carnot cycles (direct and reverse).

63. According to Boltzmann no determined time direction exists in the world so that all processes are in the end reversible, but that inside a fluctuation there is a determined direction of time: from the less probable (past) to the more probable (future) state (see in § 20 the quotation from Boltzmann's "Theory of gases"). Boltzmann and Smoluchovsky have assumed in this manner that the reversibility of physical phenomena has an absolute character. Show the fallacy of such an opinion.

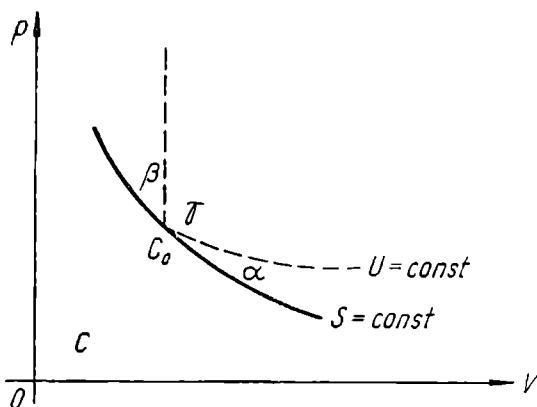


FIG. 16.

64. Show, following I. R. Plotkin, that the second law of the increase of entropy is inapplicable to the universe as a whole or to any infinite part of it.

65. On the V, p diagram (Fig. 16) through a certain state C_0 there are drawn: an adiabetic, a segment of an isochore (upwards) and a segment of a $U = \text{const}$ curve (towards the right). States not lying on the adiabetic cannot be reached from C_0 in a quasi-static adiabetic manner. Show that by means of non-static processes we can reach adiabatically from C_0 an arbitrary state of the regions α , β and γ but cannot reach states of the region C .

CHAPTER IV

METHODS OF THERMODYNAMICS

WHEN we refer to a thermodynamic method of investigation of physical phenomena we have in mind a study of these phenomena that is based on the use of the first and second laws of thermodynamics.

The application of the laws of thermodynamics for the solution of concrete physical problems is realized in thermodynamics by two methods: the method of closed-cycle processes and the method of thermodynamic potentials (or characteristic functions).

§ 21. The method of cyclical processes

1. The idea of the method of cycles consists in that, in order to establish a determined law of some phenomenon or other, one considers a reversible cycle, chosen in a suitable manner, and applies to this cycle the equation of the first law

$$\oint \delta Q = W \quad (4.1)$$

and the equation of the second law

$$\oint \frac{\delta Q}{T} = 0. \quad (4.2)$$

These equations enable us to bring to light the desired law, if the cycle chosen is such as to make it possible to evaluate the quantities needed, occurring in (4.1) and (4.2) for all elements of the cycle. If the system investigated is imagined to be made to accomplish (as is often done) Carnot's cycle, then the equation (4.2) is used in the form of the expression for the efficiency of this cycle; the efficiency found for the cycle in the concrete problem given is equated to the ratio $(T_1 - T_2)/T_1$.

2. We shall establish by means of this method the dependence of surface tension on temperature. To do this we shall consider Carnot's cycle with a liquid film in a wire frame. We shall represent this cycle on the Σ, σ diagram (Σ is the surface of the film, and σ is the surface tension) (Fig. 17). Let the film surface be equal to Σ_1 initially and the

tension be σ (the point 1 in Fig. 17). Let us stretch the film isothermally to the state 2. The surface tension will not vary in the process but, since an increase of the film surface is connected, as is shown by experiment, with cooling, then, in order that the process be carried out isothermally, the quantity of heat Q must be communicated over the section 1–2 at the temperature T . We shall further stretch the film adiabatically to the state 3; in the process the temperature will decrease by dT and the surface tension will increase by $d\sigma$. Then we shall let the film contract isothermally to the state 4 (in this connexion we have to abstract the quantity of heat Q_2), and finally we shall let the film contract further, but adiabatically, to the state 1.

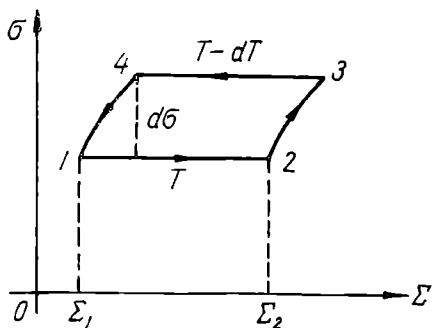


FIG. 17.

The work W accomplished by the film during a cycle is equal to $Q_1 - Q_2$. On the Σ, σ diagram this work is equal to the area of the cycle, and is negative since the cycle has been followed anticlockwise: $W = -(\Sigma_2 - \Sigma_1) d\sigma$ (as can be seen from Fig. 17, the variation of σ in an elementary adiabatic process is equal to $d\sigma$ for a certain Σ). By definition, the efficiency of the cycle is equal to

$$\eta = \frac{W}{Q_1} = -\frac{(\Sigma_2 - \Sigma_1) d\sigma}{Q_1}, \quad \text{or} \quad \eta = \frac{T - (T - dT)}{T} = \frac{dT}{T}, \quad (4.A)$$

since the film has accomplished a Carnot cycle.

By equating these two expressions we obtain

$$-\frac{(\Sigma_2 - \Sigma_1) d\sigma}{Q_1} = \frac{dT}{T}, \quad (4.B)$$

whence

$$\left(\frac{d\sigma}{dT}\right)_\Sigma = -\frac{Q_1}{\Sigma_2 - \Sigma_1} \cdot \frac{1}{T}. \quad (4.C)$$

But $Q/(\Sigma_2 - \Sigma_1) = r$ is the latent heat of formation of a unit-surface film, and therefore we obtain finally

$$\left(\frac{d\sigma}{dT}\right)_\Sigma = -\frac{r}{T}, \quad (4.3)$$

i.e. the variation of surface tension for an increase of temperature is inversely proportional to absolute temperature.

By a similar method we can also find the temperature dependence of saturated vapour pressure, the temperature dependence of an electromotive force etc. These laws, as well as (4.3), will be established by us, in the sequel, by another, simple method.†

In our course we shall also use the method of cycles in Chap. IX, for recognizing the unattainability of the absolute zero of temperature.

The example examined, as well as the problems no. 66, 67 and 68, show how in the method of cyclical processes the basic laws of thermodynamics are used and the required relationships are established.

Historically the method of cycles is the earliest method of thermodynamic investigations. Carnot, Clausius, Nernst have used only this method. The method of cyclical processes, though it can be applied in principle for the solution of any problem, has, on the other hand, a great shortcoming in that, in order to establish some relationship or other, a suitable cycle is to be chosen *ad hoc* each time: the successful solution of the problem will depend on the choice of the required cycle but, as to the choice itself, there is nothing to decide it.

Today, in nearly all cases of thermodynamic investigations another method is employed, the so-called method of thermodynamic potentials.

§ 22. The method of thermodynamic potentials

1. The method of thermodynamic potentials, or method of characteristic functions, was devised by Gibbs. It is an analytic method and is based on the use of the fundamental equation of thermodynamics

$$T dS \geq dU + \sum_i A_i da_i. \quad (4.4)$$

The idea of the method consists in that, as we shall show, the fundamental equation of thermodynamics (4.4) enables us to introduce, for a system under various conditions, certain functions of state, called thermodynamic potentials, the variation of which for a variation of state is a total differential; by using this fact such equations can be set out as are needed for the analysis of a given phenomenon.

As will be seen from the sequel, the knowledge of only one thermodynamic potential enables us to obtain both the thermic equations and the caloric equation of state as well as the properties of thermodynamic systems corresponding to these equations.

† For an application of the method of cycles to establish the above relations, as well as one more example of such method, see problems no. 66, 67 and 68.

2. To make matters easier, we shall consider at first simple systems. In this case, the fundamental equation of thermodynamics for quasi-static processes has the form

$$T dS = dU + A da \quad (4.4)$$

or, if $A = p$ and $a = V$,

$$T dS = dU + p dV. \quad (4.5)$$

This equation connects five parameters of state: T , S , U , p and V . On the other hand, the state itself of a simple system is determined by two parameters. Therefore, by selecting two of the five quantities above as the independent variables, we obtain that the fundamental equation will still contain three unknown functions, and therefore two more equations need to be added to (4.5) in order to determine them. Such equations can be the thermic and the caloric equation of state

$$p = p(T, V), \quad (4.6)$$

$$U = U(T, V). \quad (4.7)$$

Though the second law does establish a connexion between the parameters p and U in the form

$$T \left(\frac{\partial p}{\partial T} \right)_V = \left(\frac{\partial U}{\partial V} \right)_T + p, \quad (4.8)$$

this does not eliminate the need for adding to (4.5) two equations for the determination of the three unknown functions, since the relation (4.8) is a differential relation and enables us, when one of the functions is known, to determine the other, wanted function, but only in its dependence on one of the arguments, the dependence on the other argument being expressed by an arbitrary function. Therefore, owing to (4.8), in order to determine the three unknown functions in (4.5), we need to add to this equation (4.5) the thermic equation (4.6) as well as the caloric equation not in the form (4.7) but only as a function of the temperature T (a knowledge of the dependence of U on the volume V is not needed owing to (4.8)). Thus, notwithstanding (4.8), we still need to add to (4.5) two equations $p = p(V, T)$ and $U = U(T, C)$ (C is a constant quantity) and not a single equation.

However, if the independent variables are S and V , then for determining the other three variables by means of the equation (4.5), we need to know additionally not two other equations but only a single equation for the internal energy U as a function of these variables:

$$U = U(S, V). \quad (4.9)$$

In fact, by knowing (4.9), by simple differentiation we can determine, by means of (4.5) the two other thermic variables

$$T = \left(\frac{\partial U}{\partial S} \right)_V \quad (4.10)$$

and

$$p = - \left(\frac{\partial U}{\partial V} \right)_S. \quad (4.11)$$

By taking the second derivatives of $U(S, V)$ we shall obtain

$$\left(\frac{\partial^2 U}{\partial S^2} \right)_V = \left(\frac{\partial T}{\partial S} \right)_V = T \left(\frac{\partial T}{T \partial S} \right)_V = T \left(\frac{\partial T}{\partial Q} \right)_V = \frac{T}{C_V}, \quad (4.E)$$

whence

$$C_V = \frac{T}{\left(\frac{\partial^2 U}{\partial S^2} \right)_V}; \quad \left(\frac{\partial^2 U}{\partial V^2} \right)_S = - \left(\frac{\partial p}{\partial V} \right)_S = \frac{1}{V_0} \cdot \varepsilon_S. \quad (4.F)$$

and

$$\varepsilon_S = V_0 \left(\frac{\partial^2 U}{\partial V^2} \right)_S. \quad (4.G)$$

By equating the mixed derivatives $\partial^2 U / \partial S \partial V = \partial^2 U / \partial V \partial S$ we have

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial p}{\partial S} \right)_V. \quad (4.12)$$

Thus we see that the internal energy U expressed as a function of the variables S and V is a characteristic function, since in this case the other variables (T and p) are determined by differentiating U with respect to S and V . In other words the derivatives of $U(S, V)$ with respect to the characteristic variables express all the thermodynamic properties of a system: the first derivatives determine the thermic properties and the second derivatives determine the caloric properties.

The internal energy U expressed as a function of the variables S and V is also called a thermodynamic potential, since the value of pressure

$$p = - \left(\frac{\partial U}{\partial V} \right)_S \quad (4.H)$$

is expressed in terms of it, just as a force is expressed in terms of the potential energy V in mechanics ($F_x = -\partial V / \partial x$, $F_y = -\partial V / \partial y$, $F_z = -\partial V / \partial z$).

We shall observe that as a thermodynamic potential, the function $U = U(S, V)$ is inconvenient from the practical point of view, in that

one of its independent variables, the entropy S , cannot be measured directly like the quantities V , p and T .

If the independent variables are not S and V but some other quantities of a simple system, then, when expressed as a function of these other variables, the internal energy U is not a characteristic function or potential. It is found, however, that also with certain other independent variables, we can, instead of two equations

$$p = p(T, V) \quad \text{and} \quad U = U(T, C) \quad (4. J)$$

choose a single function of these variables, that will in this connexion be the characteristic function, similarly to U expressed as a function of the variables S and V .

In fact, if the independent variables of a simple system are T and V , then, by transforming† (4.5) in such a manner that the differentials dT and dV shall occur in it, and, subtracting from both sides of (4.5) the differential $d(TS)$, we shall obtain

$$-S dT = d(U - TS) + p dV; \quad (4. K)$$

by introducing the notation

$$U - TS = F, \quad (4. 13)$$

we shall have

$$dF = -S dT - p dV, \quad (4. 14)$$

whence

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad (4. 15)$$

and

$$p = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (4. 16)$$

The equation (4.16) represents the thermic equation of state; by knowing $F = F(V, T)$ we can find from (4.16) the equation $p = p(V, T)$.

The second derivatives of the function F enable us to determine the caloric quantities, i.e. the thermal capacity C_V and the compressibility coefficient β (or the isothermal modulus of elasticity $\varepsilon_T = 1/\beta$):

$$C_V = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_V, \quad (4. 17)$$

$$\beta = - \frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_T = \frac{1}{V_0 \left(\frac{\partial^2 F}{\partial V^2} \right)_T},$$

† Such a transformation of a differential form is called Legendre's transformation.

and to obtain the equation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V. \quad (4.18)$$

Thus the function F in the variables T and V is a characteristic function or thermodynamic potential. This function $F = U - TS$ is called *the free energy*. It was introduced in science by Helmholtz and is so called since, in isothermal processes, work is accomplished not at the expense of a decrease of the internal energy U (as is the case in adiabatic processes) but at the expense of a decrease of this function: $F = U - TS$, the free energy. In fact, from (4.14) for $T = \text{const}$ we have

$$p dV = -dF. \quad (4.L)$$

Therefore the free energy $F = U - TS$ has in isothermal processes the same role as the energy U in adiabatic processes. The quantity TS is called the bound energy.

If we take T and p as the independent variables, then a characteristic function will be the function $Z(T, p) = U - TS + pV$.

In fact, in the equation (4.14)

$$dF = -S dT - p dV \quad (4.M)$$

we can pass by means of a Legendre transformation to the variables T and p , by adding to both sides the differential $d(pV)$; then we shall obtain

$$d(F + pV) = -S dT + V dp, \quad (4.N)$$

or

$$dZ = -S dT + V dp, \quad (4.19)$$

where

$$Z = F + pV = U - TS + pV. \quad (4.20)$$

From (4.19) we have

$$S = -\left(\frac{\partial Z}{\partial T}\right)_p, \quad V = \left(\frac{\partial Z}{\partial p}\right)_T. \quad (4.21)$$

The second equation (4.21) enables us to find the thermic equation of state. Thus the function $Z(T, p) = U - TS + pV$ is a characteristic function in the variables T and p and is called *Gibbs' thermodynamic potential*.

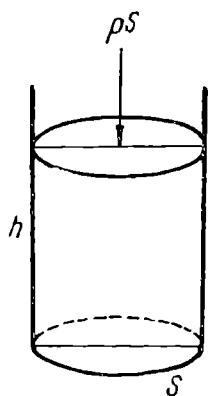


FIG. 18.

The second derivatives of $Z(T, p)$ give the thermal capacity C_p and the compressibility coefficient β

$$C_p = -T \left(\frac{\partial^2 Z}{\partial T^2} \right)_p, \quad (4.22)$$

$$\beta = -\frac{1}{V_0} \left(\frac{\partial V}{\partial p} \right)_T = -\frac{1}{V_0} \left(\frac{\partial^2 Z}{\partial p^2} \right)_T \quad (4.23)$$

and the equation

$$\left(\frac{\partial S}{\partial p} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_p. \quad (4.24)$$

Just as the decrease of free energy in isothermal processes is equal to the work of the system, the decrease of Gibbs' thermodynamic potential in isothermal processes is equal to the work of the so-called *extended system* for adiabatic processes, which for example, in the case of a gas in a closed cylinder, consists of the gas and the piston with the weight $pSh = pV$

$$E = U + pV, \quad (4.O)$$

whence

$$dE = dU + p dV + V dp = T dS + V dp. \quad (4.P)$$

In adiabatic processes the decrease of the energy of the system is equal to the work of the system, therefore

$$-(dE)_S = -V dp \quad (4.Q)$$

and hence the work of the extended system is equal to

$$\delta W_{\text{ext}} = -V dp. \quad (4.25)$$

It can be seen from (4.19) that in isothermal processes

$$-(dZ)_T = -V dp, \quad (4.R)$$

and by taking (4.25) into account we obtain

$$-(dZ)_T = \delta W_{\text{ext}}. \quad (4.26)$$

If, in addition to mechanical forces, other non-mechanical forces (electrical, magnetic etc.) also act on the system, then we can recognize also another physical meaning of the variation of the thermodynamic potential Z . In fact, let non-mechanical forces, in addition to the force of pressure, be acting on the system; then

$$T dS = dU + p dV + \delta W_{\text{n-mech}}. \quad (4.27)$$

By means of a Legendre transformation (by adding to both sides of (4.27) the differential $d(-TS + pV)$), we shall pass from the differen-

tials dS and dV to the differentials of the independent variables T and p ; then we shall obtain

$$-S dT + V dp = d(U - TS + pV) + \delta W_{\text{n-mech}} \quad (4.5)$$

and

$$dZ = -S dT + V dp - \delta W_{\text{n-mech}}, \quad (4.28)$$

whence it can be seen that in isothermal-isobaric processes in complex systems the decrease of the thermodynamic potential Z is equal to the work of non-mechanical forces acting on the system

$$-(dZ)_{p,T} = \delta W_{\text{n-mech}}. \quad (4.29)$$

The great importance of Gibbs' thermodynamic potential Z in thermodynamics derives from the fact that in an equilibrium state of a complex system (as we shall see in the séquel) the characteristic variables p and T are the same in all parts of the system and are therefore the most convenient variables in practice.

If the independent variables of a simple system are S and p , then a characteristic function will be $H(S, p) = U + pV$.

If, in fact, in the equation

$$T dS = dU + p dV \quad (4.5)$$

we pass from the differentials dS and dV to the differentials of the variables S and p (by adding to both sides of the equation (4.5) the differential $d(pV)$), we shall obtain

$$T dS + V dp = d(U + pV) \quad (4.1)$$

or

$$dH = T dS + V dp, \quad (4.30)$$

where the function

$$H = U + pV \quad (4.31)$$

is called the *enthalpy* and is a thermodynamic potential in the variables S and p , since the derivatives of $H(S, p)$ with respect to S and p give

$$T = \left(\frac{\partial H}{\partial S} \right)_p, \quad (4.32)$$

$$V = \left(\frac{\partial H}{\partial p} \right)_S; \quad (4.33)$$

$$\left(\frac{\partial^2 H}{\partial S^2} \right)_p = \left(\frac{\partial T}{\partial S} \right)_p = T \left(\frac{\partial T}{\partial Q} \right)_p = \frac{T}{C_p}$$

and

$$C_p = \frac{T}{\left(\frac{\partial^2 H}{\partial S^2}\right)_p}, \quad (4.34)$$

$$\left(\frac{\partial^2 H}{\partial p^2}\right)_s = \left(\frac{\partial V}{\partial p}\right)_s = \frac{V_0}{V_0 \left(\frac{\partial p}{\partial V}\right)_s} = -\frac{V_0}{\varepsilon_s}$$

and

$$\varepsilon_s = -\frac{V_0}{\left(\frac{\partial^2 H}{\partial p^2}\right)_s}. \quad (4.35)$$

From (4.30) we also have the equation

$$\left(\frac{\partial T}{\partial p}\right)_s = \left(\frac{\partial V}{\partial S}\right)_p. \quad (4.36)$$

The equation (4.33) is the equation of an adiabetic, so that if the enthalpy as a potential is known, then (4.33) enables us by simply differentiating H with respect to p to find the equation of the adiabetic of the system.

The physical meaning of enthalpy consists in that in isobaric processes the variation of enthalpy is equal to the quantity of heat absorbed

$$(dH)_p = (T dS)_p = (\delta Q)_p = C_p dT \quad (4.U)$$

and

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p. \quad (4.37)$$

For this reason the function H is also often called the *heat function* or *heat content*.

Since the enthalpy (4.31) is equal to the energy of the extended system, while in adiabetic processes the decrease of energy is equal to the work, then it is evident that in these processes the decrease of enthalpy of the system is equal to the work of the extended system

$$-(dH)_s = \delta W_{\text{ext}}. \quad (4.38)$$

If other, non-mechanical forces, in addition to the mechanical force of pressure, act on the system, then

$$T dS = dU + p dV + \delta W_{\text{n-mech}}, \quad (4.V)$$

$$T dS = d(U + pV) - V dp + \delta W_{\text{n-mech}},$$

and

$$dH = T dS + V dp - \delta W_{\text{n-mech}}, \quad (4.W)$$

whence it can be seen that the decrease of enthalpy (4.31) in adiabatic-isobaric processes in a complex system is equal to the work of non-mechanical forces

$$-(\delta H)_{S,p} = \delta W_{\text{n-mech}}. \quad (4.39)$$

In addition to the above four thermodynamic potentials U , F , Z and H , others can also be derived. It can easily be seen from (4.5), for example, that the entropy S is a thermodynamic potential in the independent variables U and V :

$$dS = \frac{1}{T} dU + \frac{p}{T} dV, \quad (4.X)$$

so that

$$T = \frac{1}{\left(\frac{\partial S}{\partial U}\right)_V} \quad \text{and} \quad p = \frac{\left(\frac{\partial S}{\partial V}\right)_U}{\left(\frac{\partial S}{\partial U}\right)_V}, \quad (4.Y)$$

while the volume is a thermodynamic potential in the independent variables S and U

$$dV = \frac{T}{p} dS - \frac{1}{p} dU, \quad (4.Z)$$

whence

$$p = -\frac{1}{\left(\frac{\partial V}{\partial U}\right)_S} \quad \text{and} \quad T = -\frac{\left(\frac{\partial V}{\partial S}\right)_U}{\left(\frac{\partial V}{\partial U}\right)_S} \quad (4.AA)$$

etc.

The most commonly used characteristic functions are the thermodynamic potentials U , F , Z and H and among them most often of all are used the free energy F and the thermodynamic potential Z , since the independent variables T , V and T , p , for which respectively they are potentials, can be easily measured experimentally.

3. In the case of complex systems, generalized characteristic functions can easily be found. We must proceed in this connexion from the fundamental equation of thermodynamics

$$T dS = dU + \sum_i A_i da_i. \quad (4.40)$$

If the state of a system is determined by the external parameters a_i and the entropy S , then a thermodynamic potential will be the internal energy $U(S, a_i)$ the differential of which is equal to

$$dU = T dS - \sum_i A_i da_i. \quad (4.41)$$

If the state of a system is determined by the external parameters a_i and the temperature T , then a thermodynamic potential will be the free energy $F = U - TS$, the differential of which is equal to

$$dF = -S dT - \sum A_i da_i. \quad (4.42)$$

If the state of a system is determined by assigning the variables p , T , a_1, \dots, a_n , then a thermodynamic potential will be Gibbs' thermodynamic potential $Z = U - TS + pV$ the differential of which is equal to

$$dZ = -S dT + V dp - \sum_i A_i da_i. \quad (4.43)$$

If the independent variables are p , S , a_1, \dots, a_n , then a thermodynamic potential will be the enthalpy $H = U + pV$, the differential of which is equal to

$$dH = T dS + V dp - \sum_i A_i da_i. \quad (4.44)$$

4. All these thermodynamic potentials are additive and single-valued functions of state, the decrease of which under suitable conditions determines the work of forces acting on the system. Another of their properties consists, as we shall see, in that for constant characteristic variables, extremum values of the corresponding thermodynamic potentials determine the equilibrium conditions of the system. This property can be established by proceeding from the fundamental equation (4.4) for non-static processes, when in (4.4) the inequality sign is used.

5. The thermodynamic potentials U , F , Z and H can be represented graphically in the space of the corresponding independent variables in the form of surfaces, which are usually plotted on the basis of experimental data. These surfaces, and thus also the properties of the substance itself are then investigated by means of differential geometry. Therefore geometrical methods are of great importance in thermodynamics.† One of Gibbs' important works is just called "A Method of Geometrical Representation of Thermodynamic Properties by means of Surfaces."

6. The thermodynamic potentials are related to each other, so that if some of them are known, the others can be found.

† See A. B. Mlodzeyevskii; *Geometricheskaya Termodinamika* (Geometrical Thermodynamics), Moscow University Editions (1956).

By knowing the free energy F or the thermodynamic potential Z , we can easily find the internal energy U . In the first case, from $F = U - TS$ and (4.15) we obtain

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_v. \quad (4.45)$$

In the second case from $Z = U - TS + pV$ and (4.20) and (4.21) we have

$$U = Z - T \left(\frac{\partial Z}{\partial T} \right)_p - p \left(\frac{\partial Z}{\partial p} \right)_T. \quad (4.46)$$

By knowing Z , we can also easily find the enthalpy H

$$H = U + pV = Z + TS = Z - T \left(\frac{\partial Z}{\partial T} \right)_p. \quad (4.47)$$

The equations (4.45), (4.46) and (4.47) are called the *Gibbs-Helmholtz equations*.

In the general case of a simple system when its state is determined by an external parameter a and the temperature T , we shall have, instead of equation (4.45), the Gibbs-Helmholtz equation [in the form]

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_a. \quad (4.45')$$

By integrating (4.45) or (4.47), we can find F or Z respectively from U or H . Such an evaluation, however, would give us values of F and Z in which thermodynamically undetermined constants occur. In fact, from (4.45) we have

$$\frac{U}{T^2} = \frac{F}{T^2} - \frac{1}{T} \left(\frac{\partial F}{\partial T} \right)_v = - \frac{\partial}{\partial T} \left(\frac{F}{T} \right)_v, \quad (4.48)$$

whence

$$\frac{F}{T} = - \int \frac{U}{T^2} dT + I(V), \quad (4.49)$$

where $I(V)$ is a thermodynamically undetermined quantity which depends on volume. It can be found only by having recourse to Nernst's theorem and is found to be equal to zero (see problem no. 116). Therefore we have

$$F = -T \int \frac{U}{T^2} dT. \quad (4.48)$$

Similarly from (4.47)

$$Z = -T \int \frac{H}{T^2} dT. \quad (4.49)$$

The formulae (4.48) and (4.49) enable us to determine H from U , and Z from H .

7. As can be seen from (4.10)–(4.36), by knowing at least one of the thermodynamic potentials, we can determine both the thermic and the caloric properties of a system, i.e. we can obtain complete information on its thermodynamic properties. Each thermodynamic potential contains, therefore, in itself all the characteristics of the system.

To have established the existence of such functions has meant an important advance for thermodynamics. However, if we remain within the limits of thermodynamics, this result cannot be used to its full extent. The difficulty is that the explicit form of thermodynamic potentials cannot be obtained by purely thermodynamic means, i.e. on the basis merely of the first and second law. In thermodynamics, the method of potentials consists in using the equations (4.12), (4.18), (4.24) and (4.36), which establish connexions of some properties of a system with other properties of the same system. These equations are obtained, as we have seen, from the fundamental equation of thermodynamics (4.5) and therefore are often themselves called the fundamental equations.

Only for two systems can the thermodynamic potentials be calculated: for an ideal gas and for equilibrium radiation, since we know for them both the thermic and the caloric equation of state. For all other systems, however, the thermodynamic potentials are found either from experiment or by means of statistical physics.

From this the organic connexion of thermodynamics and statistical physics is apparent. Both have one and the same object of investigation, but the investigation itself is carried out by proceeding from different initial positions. A full and thorough investigation of the properties of physical systems requires having recourse to thermodynamics and statistical physics at the same time.

In gases the thermodynamic functions are evaluated by means of the methods of statistical physics, while for liquids and solid bodies they are usually found from experiment by means of calorimetric determinations of the thermal capacities.

Let us find the expression for the internal energy U as a thermodynamic potential for an ideal (monatomic gas). It is known that the internal energy for such a gas is equal to

$$U = C_v T + U_0. \quad (4.AD)$$

This expression for U is not, however, a thermodynamic potential;

we cannot by using it determine either the thermic equation of state of an ideal gas or much else. The internal energy will be a thermodynamic potential (a characteristic function) if it is expressed as a function of the variables S and V . This can easily be done for an ideal gas since it is known that

$$S = C_v \ln T + R \ln V + S_0, \quad (4. \text{AE})$$

whence

$$T = e^{\frac{S - S_0 - R \ln V}{C_v}} = \frac{1}{V^{\gamma-1}} \cdot e^{\frac{S - S_0}{C_v}} \quad (4. \text{AF})$$

and

$$U(S, V) = \frac{C_v}{V^{\gamma-1}} \cdot e^{\frac{S - S_0}{C_v}} + U_0. \quad (4.50)$$

By using this expression for the internal energy as a thermodynamic potential, we can, in contrast to above, find by means of (4.11) and (4.10) respectively the thermic equation of state of an ideal gas $pV = RT$ and the equation of the adiabatic $pV^\gamma = \text{const.}$

For expressions of other thermodynamic potentials of an ideal gas see problem no. 73.

8. As a first example of a problem solved by the method of thermodynamic potentials, we shall establish the temperature dependence of surface tension, which we have already found by the method of cycles, in order to convince ourselves by this example of the superiority of the method of thermodynamic potentials. The result, of course, will be the same, since a determined physical relationship cannot depend on the method of investigation but is determined by the nature of the phenomenon.

We shall proceed from the expression for the differential free energy of a surface film. Let the value of the surface of the film (its external parameter a) be equal to Σ . Since the elementary work for an increase of the film surface by $d\Sigma$ is equal to $\delta W = -\sigma d\Sigma$, where σ is the coefficient of surface tension, it follows that the generalized force corresponding to the parameter Σ will be $A = -\sigma$, and the differential free energy for a film is equal to

$$dF = -S dT + \sigma d\Sigma, \quad (4. \text{AG})$$

whence

$$-\left(\frac{\partial S}{\partial \Sigma}\right)_T = \left(\frac{\partial \sigma}{\partial T}\right)_\Sigma, \quad \left(\frac{\partial \sigma}{\partial T}\right)_\Sigma = -\frac{1}{T} \left(\frac{\partial Q}{\partial \Sigma}\right)_T \quad (4. \text{AH})$$

and

$$\left(\frac{\partial \sigma}{\partial T}\right)_\Sigma = -\frac{r}{T}, \quad (4. \text{AJ})$$

which coincides with the expression (4.3) found by the method of cycles. The obtaining of this expression by the method of thermodynamic potentials reduces to finding merely the differential free energy of a film and to using the properties of a total differential.

PROBLEMS

66. By the method of cycles establish the temperature dependence of saturated vapour pressure.

67. By the method of cycles find the temperature dependence of the e. m. f. of a galvanic element.

68. By considering a cycle consisting of an isochore, an isobaric and an isothermal, determine the difference $C_p - C_V$.

69. Show that

$$\left(\frac{\partial T}{\partial p}\right)_V \left(\frac{\partial S}{\partial V}\right)_p - \left(\frac{\partial T}{\partial V}\right)_p \left(\frac{\partial S}{\partial p}\right)_V = 1 \quad (4. AK)$$

and

$$\left(\frac{\partial p}{\partial T}\right)_S \left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial p}{\partial S}\right)_T \left(\frac{\partial V}{\partial T}\right)_S = 1. \quad (4. AL)$$

70. Show that

$$C_p - C_V = T \cdot \frac{\left(\frac{\partial^2 F}{\partial T \partial V}\right)^2}{\left(\frac{\partial^2 F}{\partial V^2}\right)_T}. \quad (4. AM)$$

71. Prove the relation

$$\left(\frac{\partial p}{\partial V}\right)_S = -\frac{C_p}{C_V} \left(\frac{\partial p}{\partial V}\right)_T, \quad (4. AN)$$

by using the properties of Jacobians.

72. Prove the relation

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{\left(\frac{\partial S}{\partial V}\right)_T}{\left(\frac{\partial S}{\partial T}\right)_V}. \quad (4. AO)$$

73. Find the thermodynamic potentials F , Z and H for one mole of a monatomic ideal gas.

74. Determine the thermodynamic potentials in the independent variables p , H and T , F .

75. According to Debye's law, the thermal capacity C_V of crystals at low temperatures is proportional to the cube of the absolute temperature, $C_V = \alpha T^3$ (the coefficient α depends on the nature of the body and its volume). Show that the difference of the thermal capacities, $C_p - C_V$, of crystals for $T \rightarrow 0$ is proportional to the seventh power of temperature.

76. Evaluate the internal energy of a rarefied plasma that occupies a volume V and consists of two kinds of oppositely charged particles (N particles of each sort with charges $+e$ and $-e$).

77. Find the variation of the free energy F and of the thermodynamic potential Z of one mole of a diatomic ideal gas when this is heated from 0 to 100°C: (a) for a constant volume equal to 1 litre, (b) for a constant pressure of 1 atm.

CHAPTER V

CERTAIN APPLICATIONS OF THERMODYNAMICS

§ 23. The Gibbs-Helmholtz equation and its application to a galvanic cell

The Gibbs-Helmholtz equations (4.45) and (4.47) can be represented also in a somewhat different form that is important for a series of applications.

If a system passes isothermally from a first state where its free energy is $F_1 = U_1 + T(\partial F_1/\partial T)_V$ to a second state with free energy $F_2 = U_2 + T(\partial F_2/\partial T)_V$, the decrease of free energy obtaining in this connexion is equal to

$$F_1 - F_2 = U_1 - U_2 + T \left(\frac{\partial(F_1 - F_2)}{\partial T} \right)_V. \quad (5.A)$$

However, in a reversible isothermal process the decrease of free energy of the system, $F_2 - F_1$, is equal to the work W accomplished by the system and therefore

$$W = -\Delta U + T \left(\frac{\partial W}{\partial T} \right)_V. \quad (5.B)$$

The decrease of the internal energy $U_1 - U_2 = -\Delta U$ can be determined by proceeding from another experiment in which the system passes from a state with energy U_1 to a state with energy U_2 without accomplishing work (at a constant volume V etc.); in this case it is equal to $-\Delta U = -Q = Q_V$, namely it is equal to the quantity of heat released or to the heat effect of the transition (for example, to the heat effect of a reaction in Berthelot's bomb calorimeter). Thus we obtain the Gibbs-Helmholtz equation for an isochoric-isothermal process

$$W = Q_V + T \left(\frac{\partial W}{\partial T} \right)_V, \quad (5.1)$$

which has an important role in solving the problem of chemical affinity.

If an isothermal process takes place at a constant pressure, then to determine the work of non-mechanical forces we use the equation

$$Z = H + T \left(\frac{\partial Z}{\partial T} \right)_p. \quad (5.C)$$

The decrease of the thermodynamic potential Z in an isobaric-isothermal transition from a state 1 to a state 2 is equal to

$$Z_1 - Z_2 = H_1 - H_2 + T \left(\frac{\partial(Z_1 - Z_2)}{\partial T} \right)_p. \quad (5.D)$$

According to (4.29), $-(Z_2 - Z_1)_{T,p} = W_{\text{u-mech}}$, while $H_1 - H_2$ can be determined by proceeding from another experiment in which the system passes isobarically from a state with enthalpy H_1 to a state with enthalpy H_2 without the work of non-mechanical forces; in such a case the difference of the enthalpies, equal to $H_1 - H_2 = U_1 - U_2 + p(V_1 - V_2) = -Q = Q_p$, is the heat effect in an isobaric process.

Thus the Gibbs-Helmholtz equation for an isobaric-isothermal process assumes the form

$$W = Q_p + T \left(\frac{\partial W}{\partial T} \right)_p. \quad (5.2)$$

By means of this equation we can determine the heat of reaction of an arbitrary chemical reaction that takes place at a constant pressure, by measuring the work in the isobaric-isothermal process and determining the derivative $(\partial W / \partial T)_p$.

Let us apply equation (5.2) to a galvanic cell. We shall determine the connection between the e.m.f. of a cell and the heat of the reaction that takes place in the cell during its operation when, however, the variation of internal energy accompanying this reaction does not go into release of heat but into the work of electrical forces.

Let us consider a reversible cell in which, when current passes in the opposite direction, the reverse chemical reactions occur (for example, the Daniell cell). The Joule heat, which is proportional to the square of the intensity of current, is a quantity of the second order of smallness when the values of the intensity of current are small, and therefore the current-flowing process in the cell can be assumed to be thermodynamically reversible. The work of the cell for the passage through it of a charge e is equal to $e\mathcal{E}$ the decrease of the internal energy is equal to

the heat of reaction at a constant atmospheric pressure, Q_p , and the equation (5.2) gives

$$e\mathcal{E} = Q_p + T \cdot e \left(\frac{\partial \mathcal{E}}{\partial T} \right)_p \quad (5.E)$$

and

$$\mathcal{E} = q_p + T \left(\frac{\partial \mathcal{E}}{\partial T} \right)_p, \quad (5.3)$$

where $q_p = Q_p/e$ is the heat of reaction per unit charge. The equation (5.3) is called Helmholtz's equation for a galvanic cell.

It can be seen from this equation that the e. m. f. of a cell can be either larger or smaller than the variation of the internal energy q , depending on the sign of the temperature coefficient of the e. m. f., $(\partial \mathcal{E} / \partial T)_p$.

The term $T(\partial \mathcal{E} / \partial T)_p$ determines the quantity of heat absorbed by the cell when a unit charge flows through it: in fact, by the first law of thermodynamics, the quantity of heat Q communicated to the system (to the cell) during the passage of a charge e at a constant pressure is made up of the variation of its enthalpy ΔH and the work accomplished by the non-mechanical forces of the system (of the cell) $e\mathcal{E}$:

$$Q = \Delta H + e\mathcal{E}, \quad (5.F)$$

whence the quantity of heat absorbed by the cell for the passage of a unit charge will be

$$\frac{Q}{e} = \frac{\Delta H}{e} + \mathcal{E} = -q_p + \mathcal{E}, \quad (5.G)$$

which, according to (5.3), is equal to $T(\partial \mathcal{E} / \partial T)_p$.

If the e. m. f. of a cell increases for a temperature increase ($\partial \mathcal{E} / \partial T > 0$) then, according to (5.3), a closed cell accomplishes work not only at the expense of the decrease of internal energy accompanying the reaction but also at the expense of heat absorbed from the surrounding medium.† Such a cell working adiabatically will cool.

If, on the contrary, the temperature coefficient of the e.m.f. $\partial \mathcal{E} / \partial T$ is negative, then in such a cell the chemical energy is partly converted into work and partly goes either into an increase of temperature when the cell works under adiabatic conditions, or is ceded in

† The efficiency of such a cell (the ratio of work to the heat effect of the reaction) is greater than unity.

the form of heat to the surrounding medium when the cell works under isothermal conditions.

By Faraday's law of electrolysis the quantity of electricity e that passes through a cell is proportional to the number n of reacting moles of the electrolyte and to the valency z of the ion that carries the charge

$$e = Fnz, \quad (5. H)$$

where the proportionality coefficient $F = 96,540$ Coulomb/mole (Faraday's number). Therefore Helmholtz's equation assumes the form

$$\mathcal{E} = \frac{Q_p}{zF} + T \left(\frac{\partial \mathcal{E}}{\partial T} \right)_p, \quad (5.4)$$

where Q_p is the heat of reaction per mole of the reacting substance. Concerning the dependence of the e. m. f. of a cell on the external pressure see problem no. 79.

§ 24. The cooling of gas in reversible and irreversible adiabatic expansion. The Joule-Thomson effect. Kapitza's turbo-cooler

A problem which is very important in practice is the liquefaction of gases. To solve this problem it is necessary to decrease the velocity of motion of the gas molecules and to make them closer to each other. The latter is achieved by compressing the gas by means of compressors, while to decrease the temperature the gas is made to accomplish work by adiabatic expansion. The expansion process itself can occur both reversibly and irreversibly. We shall consider the cooling of a gas in either case.

1. The variation of temperature in an irreversible adiabatic expansion occurs, as we shall see, owing to departure of real gases from the behaviour of ideal gases and is referred to as the *Joule-Thomson effect*.

Let us consider the theory of this effect. In an adiabatically insulated cylinder (Fig. 19) gas is made to pass from a region with a high pres-

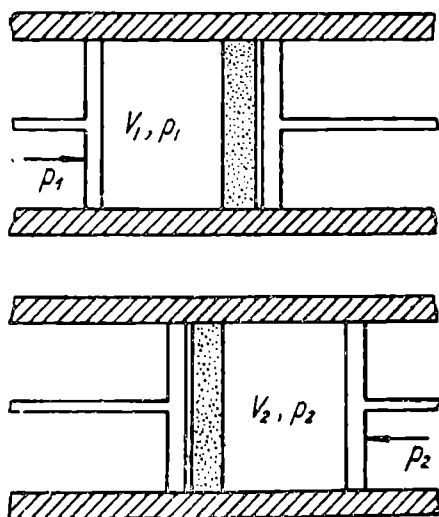


FIG. 19.

sure p_1 through a porous diaphragm† to a region with a lower pressure p_2 . In such an expansion of a gas with a pressure decrease ($\Delta p = p_2 - p_1 < 0$) there occurs a variation of temperature. For a small pressure gradient ($|\Delta p|/p_1 \ll 1$) this phenomenon is called the Joule-Thomson differential effect, while for a large pressure gradient it is called the integral effect.

Let us evaluate the magnitude of the differential effect which is described by the Joule-Thomson coefficient $\mu = \Delta T/\Delta p$.

Since the process is adiabatic, then, by the first law, the decrease of internal energy is equal to the work of the gas (on the left of the diaphragm work is accomplished on the gas, and on the right it is the gas which accomplishes work by pushing the contiguous layers at the constant pressure p_2) and therefore

$$U_1 - U_2 = p_2 V_2 - p_1 V_1. \quad (5.5)$$

As to the kinetic energy of the gas and the loss due to friction in the porous diaphragm, these are negligibly small for a small velocity of flow since they are proportional to the square of this velocity. From (5.5) we obtain

$$U_1 + p_1 V_1 = U_2 + p_2 V_2, \quad (5.J)$$

i.e. the *Joule-Thomson process is isoenthalpic*

$$\Delta H = H_2 - H_1 = 0. \quad (5.6)$$

This enables us to find μ easily.

In fact, as $\Delta H = 0$, while Δp and ΔT are small in the Joule-Thomson differential effect, then, by retaining linear terms only, we have

$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_p \Delta T + \left(\frac{\partial H}{\partial p}\right)_T \Delta p, \quad (5.K)$$

whence

$$\mu = \frac{\Delta T}{\Delta p} = - \frac{\left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}. \quad (5.L)$$

From $dH = TdS + Vdp$ we find

$$\left(\frac{\partial H}{\partial p}\right)_T = T \left(\frac{\partial S}{\partial p}\right)_T + V, \quad \left(\frac{\partial H}{\partial T}\right)_p = C_p. \quad (5.M)$$

† Owing to friction, flow in this diaphragm is not turbulent, and the gas on both sides of it is homogeneous.

But, from $dZ = -SdT + Vdp$ it follows that

$$\left(\frac{\partial S}{\partial p}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_p, \quad (5.N)$$

and therefore

$$\frac{\Delta T}{\Delta p} = \frac{T\left(\frac{\partial V}{\partial T}\right)_p - V}{C_p}. \quad (5.7)$$

The derivative $(\partial V/\partial T)_p$ occurring here can be found from the thermic equation of state.

For an ideal gas $V = RT/p$, $(\partial V/\partial T)_p = R/p$, and from (5.7) we obtain $\Delta T = 0$, which expresses Joule's law.

In the case of a van der Waals' gas, by differentiating the equation

$$\left(p + \frac{a}{V^2}\right)(V - b) = RT \quad (5.O)$$

with respect to T at a constant p , we have

$$-\frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_p(V - b) + \left(p + \frac{a}{V^2}\right)\left(\frac{\partial V}{\partial T}\right)_p = R, \quad (5.P)$$

whence

$$\left(\frac{\partial V}{\partial T}\right)_p = \frac{R}{p + \frac{a}{V^2} - \frac{2a}{V^3}(V - b)} = \frac{R(V - b)}{RT - \frac{2a}{V^3}(V - b)^2}. \quad (5.8)$$

By assuming the gas not to be very dense and neglecting in (5.8) quantities of the second order with respect to a and b we shall obtain

$$\begin{aligned} \left(\frac{\partial V}{\partial T}\right)_p &\approx \frac{V - b}{T\left(1 - \frac{2a}{RTV}\right)} = \frac{V}{T}\left(1 - \frac{b}{V}\right)\left(1 + \frac{2a}{RTV}\right) \approx \\ &\approx \frac{V}{T}\left(1 - \frac{b}{V} + \frac{2a}{RTV}\right). \end{aligned} \quad (5.9)$$

By substituting (5.9) in (5.7) we shall have

$$\frac{\Delta T}{\Delta p} = \frac{2a/RT - b}{C_p} \quad (5.10)$$

from which it can be seen that the temperature variation of a van der Waals' gas in an irreversible adiabatic expansion is caused by its departure from the ideal state ($a \neq 0$, $b \neq 0$). The result of the Joule-

Thomson effect itself for a not very dense gas depends on the relation between the quantities a and b which have an opposite influence on the sign of the effect.

If the interaction forces between molecules are large so that the pressure correction predominates and b can be taken equal to zero, then

$$\frac{\Delta T}{\Delta p} = \frac{2a}{RT C_p} > 0, \quad (5.Q)$$

i.e. the gas will cool ($\Delta T < 0$, since $\Delta p < 0$).

If the molecular interaction forces are small ($a \rightarrow 0$) and the volume correction predominates, then

$$\frac{\Delta T}{\Delta p} = -\frac{b}{C_p} < 0, \quad (5.R)$$

i.e. the gas will warm up ($\Delta T > 0$).

In the first case the expanding gas accomplishes work against the internal forces and this lowers its temperature, while in the second case ($a \rightarrow 0$) the work done on the gas $p_1 V_1 - p_2 V_2$ is found to be positive and goes to increasing its internal energy—the gas warms up. At a certain temperature the coefficient μ for a real gas is equal to zero and the gas behaves as an ideal gas. This will occur when $(2a/RT) - b = 0$, i.e. at a temperature T_i

$$T_i = \frac{2a}{Rb}, \quad (5.11)$$

which is called the *inversion temperature*. At this temperature the Joule-Thomson effect changes its sign: below the inversion temperature the effect is positive ($\mu > 0$, the gas cools) and above T_i the effect is negative ($\mu < 0$, the gas warms up). In all gases the inversion temperature is considerably higher than the critical temperature.

In hydrogen and inert gases the cohesion forces between particles are small and therefore at ordinary temperatures these gases warm up. The inversion temperature in hydrogen is -57°C ; the lowest inversion temperature is that of helium: -239°C (at atmospheric pressure). In order to cool helium and liquefy it by the Joule-Thomson method, its temperature must be preliminarily lowered to a value below -239°C , which is done by means of boiling hydrogen.

2. Let us consider now, the cooling of a gas in a reversible adiabatic expansion with production of external work.

The apparatus used in refrigerating machines where this work is accomplished is called an expansion cooler; its main part, the piston, is put in motion by the gas to be cooled.

Since the very beginning of the twentieth century attempts were made to construct deep-freezing machines and, in particular, to replace the reciprocating engines in the expansion cooler by more economical and efficient engines, namely turbines. For a long time these attempts met with failure since all the calculations for the turbines were carried out by treating the fluid as a vapour. Academician Kapitsa was the first to express the opinion that if air is cooled to very low temperatures it becomes so dense that its properties are closer to those of a liquid than to those of a vapour. In 1935, by proceeding from this, Kapitsa developed a turbo-cooler of novel design similar in type to a water turbine rather than a vapour turbine, with an efficiency of more than 0.85.

The introduction, in the cooler, of turbines, in the place of piston engines, and of a turbo-compressor, instead of the multi-stage compressor used to compress the gas in former apparatus, has made possible the liquefaction of gases at relatively low pressures (6–8 atm).

We can easily find the temperature variation of a gas in a reversible adiabatic expansion. From

$$\delta Q = dU + p dV = dH - V dp = \left(\frac{\partial H}{\partial T}\right)_p dT + \left[\left(\frac{\partial H}{\partial p}\right)_T - V\right] dp = 0 \quad (5.S)$$

we find

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{V - \left(\frac{\partial H}{\partial p}\right)_T}{\left(\frac{\partial H}{\partial T}\right)_p}, \quad (5.T)$$

or

$$\left(\frac{\partial T}{\partial p}\right)_s = \frac{T \left(\frac{\partial V}{\partial T}\right)_p}{C_p}. \quad (5.12)$$

Since in every gas $(\partial V/\partial T)_p$ is positive, it follows that in an adiabatic reversible expansion $(\partial T/\partial p)_s$ is positive, i.e. a gas is always cooled ($dT < 0$ since $dp < 0$), independently of the form of its equation of state. This makes it advantageous, in principle, to use the reversible adiabatic expansion of gases for their cooling and liquefaction in comparison with the Joule–Thomson process.

Owing, however, to the difficulty of realizing in engineering practice a reversible adiabatic expansion, the main method today of obtaining low temperatures is still the method of irreversible gas expansion.

§ 25. The thermodynamics of dielectrics and magnetic substances

Let us consider the behaviour of physical systems on which, in addition to pressure, there also act non-mechanical forces, for example an electric or magnetic field.

1. As is well known, the elementary work per unit volume of a dielectric, which is accomplished in the motion of the charges that generate the field in the dielectric is equal to

$$\delta W = -\frac{1}{4\pi} (E, dD), \quad (5.13)$$

and, for an isotropic dielectric, is equal to $\delta W = -EdD/4\pi$.

The quantity D which in the case considered has the role of an external parameter is not so for the dielectric itself. Therefore δW is not the polarization work of the dielectric in its true sense, i.e. in the sense of work for generating polarization by the displacement of charges in the molecules of the dielectric and for giving rise to a preferred orientation of these molecules.† In order to find the value of the work of polarization of the dielectric in the true sense, we transform the expression (5.13) to a form in which the independent variable is the external parameter of the dielectric, namely the electric field E . Since to this external parameter there correspond two internal (electric) parameters of the dielectric, the polarization P and the induction D , then the required transformation of the expression (5.13) can be carried out in two ways:

$$\delta W = -d\left(\frac{E^2}{8\pi}\right) - d(PE) + P dE \quad (5.14)$$

and

$$\delta W = -d\left(\frac{E^2}{8\pi}\right) - d(PE) + \frac{1}{4\pi} D dE. \quad (5.15)$$

The first term on the right-hand side of (5.14) can be interpreted as the work for engendering the electric field in a vacuum, the quantity $d(PE)$ can be interpreted as the work against the external electric

† The expression (5.13) represents the work of a certain extended system, similarly to the work (4.25) for a system consisting of a gas and a piston with a weight.

field, and the third term can be interpreted as the polarization work in its true sense when the internal parameter of the dielectric associated with its external parameter E is the polarization P . Similarly the third term in the right-hand side of (5.15) can be interpreted as the polarization work in its true sense when D is the internal parameter of the dielectric associated with E .

Since, however, the polarization of a dielectric in a field is indissolubly connected with the arising of the potential energy— PE of the dielectric in this field, then one usually takes as the true polarization work (of a dielectric) the quantity

$$\delta W_{\text{proper}} = P dE + d(-PE) = \delta W + d\left(\frac{E^2}{8\pi}\right) = -E dP \quad (5.16)$$

$$(a = P, \quad A = -E).$$

Then the polarization work PdE is equal to the sum of the true polarization work δW_{proper} and the work against the external field $d(PE)$

$$\delta W_{\text{polarization}} = P dE \quad (a = E, \quad A = P), \quad (5.17)$$

while the polarization work $DdE/4\pi$ is equal to the work $\delta W_{\text{polar.}}$ without the work for generating the field in a vacuum— $d(E^2/8\pi)$

$$\delta W' = \frac{1}{4\pi} D dE \quad \left(a = E, \quad A = \frac{1}{4\pi} D\right). \quad (5.18)$$

Similarly for a unit volume of a magnetic substance

$$\delta W = -\frac{1}{4\pi} H dB, \quad (5.19)$$

$$\delta W_{\text{proper}} = -H dM, \quad (5.20)$$

$$\delta W_{\text{polarization}} = M dH, \quad (5.21)$$

$$\delta W' = \frac{1}{4\pi} B dH. \quad (5.22)$$

Therefore the fundamental equation of thermodynamics for a dielectric in an electric field will be:

(a) in terms of the independent (electric) variable D

$$T dS = dU + p dV - \frac{1}{4\pi} E dD; \quad (5.23)$$

(b) in terms of the independent variable P

$$T dS = dU_{\text{proper}} + p dV - E dP, \quad (5.24)$$

where $U_{\text{proper}} = U - (E^2/8\pi)$ is the internal energy "proper"† per unit volume of dielectric (U without the energy of the field in a vacuum);

(c) in terms of the independent variable E , when the quantity associated with it is the polarization vector P ,

$$T dS = dU_{\text{polarization}} + p dV + P dE, \quad (5.25)$$

where $U_{\text{polarization}}$ is equal to $U_{\text{proper}} + (-PE)$, i.e. is the sum of the internal energy, proper, of polarization of the dielectric and its potential energy in the electric field;

(d) in terms of the independent variable E , when the quantity associated with it is the induction D ,

$$T dS = dU' + p dV + \frac{1}{4\pi} D dE, \quad (5.26)$$

where $U' = U - (ED/4\pi) = U_{\text{polarization}} - E^2/8\pi$ is the internal energy of the dielectric taking into account its potential energy in the field without the energy of the field in a vacuum.

The choice of one or other electrical independent variable will depend on the nature of the problem considered and corresponds to investigating a system having determined internal energy U , U_{proper} , $U_{\text{polarization}}$ and U' .

Similar expressions for magnetic materials can be obtained simply by replacing electrical quantities by magnetic ones.

By using any one of the fundamental equations of thermodynamics for dielectrics (5.23)–(5.26), expressions can easily be obtained for the differentials of thermodynamic potentials. Thus from (5.23) we have

$$\left. \begin{aligned} dU &= T dS - p dV + \frac{1}{4\pi} E dD, \\ dF &= -S dT - p dV + \frac{1}{4\pi} E dD, \\ dZ &= -S dT + V dp - \frac{1}{4\pi} D dE, \\ dH &= T dS + V dp - \frac{1}{4\pi} D dE. \end{aligned} \right\} \quad (5.27)$$

† The internal energy $U - (E^2/8\pi)$ is referred to as U_{proper} only conventionally, since E is the field already modified by the presence of the dielectric.

Similarly from (5.24) we obtain

$$\left. \begin{aligned} dU &= T dS - p dV + E dP, \\ dF &= -S dT - p dV + E dP, \\ dZ &= -S dT + V dp - P dE, \\ dH &= T dS + V dp - P dE \end{aligned} \right\} \quad (5.28)$$

(where U , F , Z and H denote here respectively U_{proper} , F_{proper} , Z_{proper} and H_{proper}).

These expressions are the basis of the thermodynamics of dielectrics (and of magnetic materials when the electric quantities are replaced by the corresponding magnetic ones).

2. Let us evaluate the free energy per unit volume of a dielectric that is found in an electric field.

When the independent variable is the induction D (for example, in the displacement of the charges that generate the field) the expression for the differential of free energy must be taken from (5.27). By integrating this expression at constant temperature and volume for dielectrics having a linear thermic equation of state (for the electric quantities D and E) $D = \varepsilon E$ we shall obtain

$$F(T, D) = F_0 + \frac{D^2}{8\pi\varepsilon}, \quad (5.29)$$

where F_0 is the free energy of the dielectric in the absence of a field.

It can be seen from (5.29) that, in the polarization of a dielectric in an electric field at constant temperature and volume, the variation of its internal energy is equal to the energy of the electric field in the dielectric

$$\frac{D^2}{8\pi\varepsilon} = \frac{\varepsilon E^2}{8\pi} = \frac{ED}{8\pi}. \quad (5.U)$$

By omitting in (5.29) F_0 which is independent of the field, we shall obtain

$$F(T, D) = \frac{D^2}{8\pi\varepsilon} = \frac{\varepsilon E^2}{8\pi}. \quad (5.30)$$

The free energy, proper, for unit volume of dielectric, connected with the presence of a field is evidently equal to

$$F_{\text{proper}}(T, D) = F(T, D) - \frac{E^2}{8\pi} = \frac{\varepsilon - 1}{8\pi} E^2. \quad (5.31)$$

This expression can also be obtained by integrating the equation for dF_{proper} from (5.28) at constant values of T and V

$$F_{\text{proper}}(T, P) = \int_0^P E dP = \frac{\varepsilon - 1}{8\pi} E^2, \quad (5.V)$$

since $P = (\varepsilon - 1)E/4\pi$.

The variation of internal energy of a dielectric during the time of its polarization at constant temperature and volume can be found from the Gibbs-Helmholtz equation (4.45) with the external parameter $\alpha = D$:

$$U(T, D) = F(T, D) - T \left(\frac{\partial F}{\partial T} \right)_D. \quad (5.W)$$

By using (5.30) we obtain

$$U(T, D) = \frac{D^2}{8\pi} + \frac{TD^2}{8\pi\varepsilon^2} \cdot \frac{\partial \varepsilon}{\partial T} = \frac{E^2}{8\pi} \left(\varepsilon + T \frac{\partial \varepsilon}{\partial T} \right). \quad (5.32)$$

The internal energy, proper, per unit volume of dielectric $U_{\text{proper}}(T, D)$ is evidently equal to

$$U_{\text{proper}}(T, D) = U(T, D) - \frac{E^2}{8\pi} = \frac{E^2}{8\pi} \left(\varepsilon - 1 + T \frac{\partial \varepsilon}{\partial T} \right), \quad (5.33)$$

which also follows directly from the Gibbs-Helmholtz equation

$$U_{\text{proper}}(T, P) = F_{\text{proper}}(T, P) - T \left(\frac{\partial F_{\text{proper}}}{\partial T} \right)_P. \quad (5.X)$$

It can be seen from (5.32) that the internal energy of a dielectric $U(T, D)$ connected with the presence of a field is not equal to the energy of the electric field in the dielectric $\varepsilon E^2/8\pi$. This is explained by the fact that, in electro-dynamics, by the field energy $\varepsilon E^2/8\pi$ is meant all the energy that must be expended for generating the field in the dielectric *at constant temperature* (and not constant entropy!), whereas the expression $U(T, D)$ determines the variation of internal energy of a dielectric for its polarization, also at a constant temperature, but allowing for the energy ceded to the thermostat if the polarization causes a variation of temperature of the dielectric. As a consequence of this, the internal energy proper connected with polarization, $U_{\text{proper}}(T, D)$, of a dielectric can prove to be exactly equal to zero. For example, in the particular case of an ideal dipolar gas, for which according to Curie's law $\varepsilon = 1 + (C/T)$ (C is Curie's constant), the internal energy $U(T, D)$ is equal, according to (5.33), to $E^2/8\pi$, i.e. to the energy of

the field in a vacuum. Therefore the internal energy proper $U_{\text{proper}}(T, D)$ of such a gas is evidently equal exactly to zero: $U_{\text{proper}}(T, D) = U(T, D) - (E^2/8\pi) = 0$.

In the light of what has been expounded above this result is not unexpected. It can be seen from the electrodynamical definition of field energy that the quantity $\varepsilon E^2/8\pi$ is not the energy but the free energy of the field in the dielectric. As (5.30) shows, it is exactly coincident with the free energy of a polarized dielectric; on the other hand, the internal energy of a field in the thermodynamic sense coincides with the internal energy of a dielectric in the field, (5.32). It is easy to see that the integration of the equation (5.27) for dU for assigned entropy and volume does not give for the variation of energy of a dielectric, that satisfies the linear relationship $D = \varepsilon E$, the quantity $D^2/8\pi\varepsilon$

$$U(S, D) - U_0 = \frac{1}{4\pi} \int_0^D \frac{1}{\varepsilon} D \, dD \neq \frac{D^2}{8\pi\varepsilon}, \quad (5.Y)$$

since in the adiabatic variation of the induction D the temperature of the dielectric does not in general remain constant and ε can no longer be considered as a constant. Only in the particular case when ε does not depend on temperature, we have

$$F(T, D) - F_0 = U(S, D) - U_0 = \frac{\varepsilon E^2}{8\pi}, \quad (5.Z)$$

and the energy of the field coincides with its free energy.

From the fundamental equation of thermodynamics for dielectrics (5.26) in terms of the independent (electric) variable E we obtain

$$dF' = -S \, dT - p \, dV - \frac{1}{4\pi} D \, dE. \quad (5.34)$$

By integrating (5.34) at constant temperature and volume for dielectrics that satisfy the linear relationship $D = \varepsilon E$, we shall have (by neglecting quantities independent of the field):

$$F'(T, E) = -\frac{\varepsilon E^2}{8\pi} \quad (5.35)$$

and

$$F'_{\text{proper}}(T, E) = F'(T, E) - \left(-\frac{E^2}{8\pi}\right) = -\frac{\varepsilon - 1}{8\pi} E^2. \quad (5.36)$$

By comparing (5.30) with (5.35) and (5.31) with (5.36) we observe that the potentials $F(T, D)$ and $F'(T, E)$ and also $F_{\text{proper}}(T, D)$ and $F'_{\text{proper}}(T, E)$ differ from each other only in their sign

$$\left. \begin{aligned} F(T, D) &= -F'(T, E) = \frac{\varepsilon E^2}{8\pi}, \\ F_{\text{proper}}(T, D) &= -F'_{\text{proper}}(T, E) = \frac{\varepsilon - 1}{8\pi} E^2, \end{aligned} \right\} \quad (5.37)$$

which is similar to the relation, known from electrodynamics, between the variation of field energy (i.e. of the free energy of the field, as has been established above) of conductors in a vacuum $\delta_\varphi U$ (occurring for constant potentials φ of the conductors) and its variation $\delta_e U$ (arising for constant charges e of the conductors): $\delta_\varphi U = -\delta_e U > 0$. Such a connexion between $\delta_\varphi U$ and $\delta_e U$ (and not their equality) is due, as is known, to the fact that if for constant potentials of the conductors and for a variation of their charges the work of the forces of the field is accomplished at the expense of the energy of the external e.m.f.'s (which maintain these potentials constant), then for constant charges and varying potential of the conductors the work of the forces of the field is accomplished at the expense of the energy of the field.

Similarly to this, the relations (5.37) arise from the fact that whereas $F(T, D)$ determines the variation of free energy of the dielectric (or the variation of free energy of the field in the dielectric) at the expense of positive work of the external sources displacing the charges in the field, the expression $F'(T, E)$ determines the variation of free energy of the dielectric (or the variation of free energy of the field in a dielectric) for generating the field in the dielectric by allowing for the work against the external sources.

The above analogy between $\delta_\varphi U$ and $\delta_e U$ on the one hand and $F(T, D)$ and $F(T, E)$ on the other, enables us to clarify which formulation of the problem corresponds to the choice of the independent variable D and which to the choice of the independent variable E .

3. Magnetostriction, electrostriction and piezoelectric effect

The expressions (5.27) and (5.28) for the differentials of the thermodynamic potentials of dielectrics (and the analogous expressions for magnetic materials) enable us to establish a number of relations between various properties of dielectrics and magnetic materials.

Thus, from the expression for the thermodynamic potential per unit volume of a magnetic material

$$dZ = -S dT + V dp - M dH \quad (5.38)$$

we find

$$\left(\frac{\partial V}{\partial H}\right)_{p,T} = -\left(\frac{\partial M}{\partial p}\right)_{T,H}. \quad (5.39)$$

Here $(\partial V/\partial H)_{p,T}$ is the variation of volume of magnetic material caused by the magnetic field and is called volume magnetostriction; the quantity $(\partial M/\partial p)_{T,H}$ determines the variation of magnetization for a pressure variation, called the piezomagnetic effect. The relation (5.38) connects these two magnetothermic phenomena.

From the relation

$$dZ = -S dT + V dp - P dE \quad (5.40)$$

we find in a similar manner for dielectrics the connexion between electrostriction $(\partial V/\partial E)_{p,T}$ and the piezoelectric effect $(\partial P/\partial p)_{E,T}$, i.e.

$$\left(\frac{\partial V}{\partial E}\right)_{p,T} = -\left(\frac{\partial P}{\partial p}\right)_{E,T}. \quad (5.41)$$

The formula (5.41), just as (5.39), also corresponds to volume piezo-effect, though piezoelectric phenomena are usually observed in crystals in determined crystallographic directions. A slab cut from a piezoelectric crystal and provided with a pair of electrodes undergoes a deformation under the action of an external electric field, which fact causes in it elastic oscillations. Vice versa, a deformation induced mechanically causes electric charges on the electrodes of the slab.

Piezoelectric crystals find wide application in radio engineering, electro-acoustics and ultrasonic acoustics and in many other branches of science and engineering, connected with the transformation of periodic electrical processes into mechanical processes and vice versa.

4. *Magnetic and nuclear cooling*

The cooling of a body can be caused not only by adiabatic expansion but also by an arbitrary adiabatic work of the system. Thus, according to a suggestion by Debye (1926) the adiabatic demagnetization of paramagnetic crystals is employed as one of the basic methods for obtaining ultra-low temperatures ($T < 1^\circ\text{K}$).

The phenomenon of temperature variation in adiabatic demagnetization is called the magnetocaloric effect. The quantitative value of

this effect $(\partial T/\partial H)_S$ can be found from the expression of the differential of enthalpy I of a magnetic material situated in a magnetic field H

$$dI = T dS + V dp - M dH. \quad (5. AA)$$

In fact, we obtain from this expression

$$\left(\frac{\partial T}{\partial H}\right)_{p,S} = -\left(\frac{\partial M}{\partial S}\right)_{p,H} = -\left(\frac{\partial M}{\partial T}\right)_{p,H} \cdot \frac{1}{\left(\frac{\partial S}{\partial T}\right)_{p,H}} \quad (5. AB)$$

but

$$\left(\frac{\partial S}{\partial T}\right)_{p,H} = \frac{1}{T} \left(\frac{\partial Q}{\partial T}\right)_{p,H} = \frac{C_{p,H}}{T}. \quad (5. AC)$$

Therefore

$$\left(\frac{\partial T}{\partial H}\right)_{p,S} = -\frac{T}{C_{p,H}} \cdot \left(\frac{\partial M}{\partial T}\right)_{p,H}. \quad (5. AD)$$

In paramagnetic materials $M = \kappa H$, and the magnetic susceptibility κ by Curie's law is inversely proportional to temperature

$$\kappa = \frac{C}{T} \quad (5. 42)$$

(C is Curie's constant, $C > 0$). From (5.42) we have

$$\left(\frac{\partial M}{\partial T}\right)_{p,H} = H \left(\frac{\partial \kappa}{\partial T}\right)_{p,H} = -\frac{HC}{T^2} \quad (5. AE)$$

and therefore

$$\left(\frac{\partial T}{\partial H}\right)_{p,S} = \frac{CH}{C_{p,H} T}. \quad (5. 43)$$

Hence it can be seen that in demagnetization ($dH < 0$) temperature is lowered ($dT < 0$). By Debye's law the thermal capacity at low temperatures is proportional to the cube of temperature

$$C_{p,H} = \alpha T^3, \quad (5. AF)$$

and therefore

$$\left(\frac{\partial T}{\partial H}\right)_{p,S} \sim \frac{1}{T^4}, \quad (5. AG)$$

Thus at low temperatures the variation of temperature can be very large, inversely proportional to the fourth power of temperature.

In a number of laboratories temperatures of the order of 0.001°K

have been obtained by the method of magnetic cooling.† The lowest temperature that can be obtained in practice by this method is determined by the presence of interaction between electron spins (dipole-to-dipole interaction, exchange interaction etc.).

Shortly after the first successful experiments on magnetic cooling the suggestion was advanced (1934–1935) that by demagnetizing systems of nuclear spins considerably lower temperatures could be achieved for which the ordering of nuclear spins takes place. In general, the lower the temperatures one wants to obtain the weaker the interactions in the working substance that one has to use.

First tentative experiments carried out recently (1956) have shown that by using nuclear demagnetization, spin temperatures of the order of 10^{-6}°K can be obtained. These experiments have enabled us by a direct method to obtain data on the interaction between nuclei in metals.‡

§ 26. Radiation thermodynamics

The laws of thermodynamics have universal application: they are applicable to both classical and quantum systems, to both matter and field, and first of all to the electromagnetic field, i.e. to radiation.

Radiation that is found in a certain region of space in equilibrium with surrounding bodies is called *equilibrium radiation*. The temperature of two bodies in equilibrium is, as is well known, the same. Since radiation is not “radiant energy”, as it is sometimes called, but a form of matter, then, just as any other body, radiation that is found in equilibrium with other bodies has the temperature of these bodies.††

From the viewpoint of thermodynamics equilibrium radiation is a system characterized by a volume V , temperature T and pressure p .

From the microscopic viewpoint equilibrium radiation is a continuous aggregate of electromagnetic waves (having frequencies from 0 to ∞) radiated by randomly moving particles of the surrounding bodies. The amplitudes and phases of these waves in the case of such

† The working body (the paramagnetic salt) used is iron-ammonium alum. Although the magnetic cooling method suggested by Debye in 1926 has found wide practical application, continuously (cyclically) acting magnetic refrigerating machines could be made only in 1954 (see *Uspekhi fiz. nauk.* 51, No. 2, 303, (1957)).

‡ See article by N. Kurti, F. N. Robinson, F. Simon and D. A. Spor, “Nuclear cooling” (*Uspekhi fiz. nauk.* 51, No. 2, 45, (1957)).

†† The notion of temperature of equilibrium radiation was firstly expressed in 1893 by the Russian physicist B. B. Golitsyn, and this has enabled us fully to apply thermodynamics to radiation.

“natural” radiation are distributed over the whole spectrum in a perfectly random manner.

Let $u_\nu d\nu$ be the wave energy per unit volume in the frequency interval $\nu, \nu + d\nu$ (u_ν is called the spectral density of radiation energy). Then the total energy per unit volume of equilibrium radiation is equal to

$$u = \int_0^\infty u_\nu d\nu, \quad (5.44)$$

and, owing to isotropicity, the total energy of radiation in a volume V will be

$$U = uV. \quad (5.4H)$$

Similarly, if $s_\nu d\nu$ is the entropy of a unit volume of radiation with frequencies in the interval $\nu, \nu + d\nu$, then the total specific entropy of equilibrium radiation is equal to

$$s = \int_0^\infty s_\nu d\nu, \quad (5.45)$$

and the entropy of radiation in a volume V will be

$$S = sV. \quad (5.4J)$$

If the energy of waves with frequencies in the interval $\nu, \nu + d\nu$, radiated in a unit time by a unit surface of a body is equal to $\epsilon_\nu d\nu$, then ϵ_ν is called the *radiant emissivity* of this body in the given frequency interval at a determined temperature.

If radiant energy $I_\nu d\nu$ in the frequency interval $\nu, \nu + d\nu$ is incident on a body, then in general a portion of this energy, $I_{\nu A} d\nu$ is absorbed, a portion $I_{\nu R} d\nu$ is reflected and a portion $I_{\nu D} d\nu$ is transmitted by the body, the following evident relations being satisfied

$$I_{\nu A} d\nu + I_{\nu R} d\nu + I_{\nu D} d\nu = I_\nu d\nu \quad (5.4K)$$

and

$$\frac{I_{\nu A}}{I_\nu} + \frac{I_{\nu R}}{I_\nu} + \frac{I_{\nu D}}{I_\nu} = 1. \quad (5.46)$$

The first term of this sum $I_{\nu A}/I_\nu = A_\nu$ is called the *absorptivity* of the body, the second term $I_{\nu R}/I_\nu = R_\nu$ is called the *reflectivity* and $I_{\nu D}/I_\nu = D_\nu$ is called the *transmittivity*. All these quantities are referred to a unity frequency interval from ν to $\nu + d\nu$, are dimensionless, and can vary in the interval from zero to unity since, according to (5.46)

$$A_\nu + R_\nu + D_\nu = 1. \quad (5.47)$$

Bodies that absorb all rays of whatever frequency incident on them ($A_\nu = 1$ and $R_\nu = D_\nu = 0$) are called *absolutely black* (or simply black); bodies that reflect all radiation incident on them ($R_\nu = 1$, $A_\nu = D_\nu = 0$) are called *specular* or *white*, and bodies that transmit all incident radiation ($D_\nu = 1$, $A_\nu = R_\nu = 0$) are called *absolutely transparent*.

In nature there are no bodies with such absolute properties, but many bodies can be approximately attributed to one or other class. For example, soot is approximately black ($A_\nu = 0.95$) and platinum-black is even blacker. An absolutely black body was realized in 1895 according to a suggestion by Wien and Lummer in the form of an aperture in a closed cavity: radiation incident on such a "body" is totally absorbed by it.

Inside a cavity with specular walls there is no radiation if there are no bodies in it, however high the temperature of the envelope, since such walls do not radiate at all. However, if we open a door in the wall and let in from without radiation of various frequencies from bodies at different temperatures,† then this arbitrary radiation introduced in the cavity will remain there without any variation, since it cannot either be increased at the expense of emission, or decreased by means of absorption, or varied owing to interaction between rays since by the superposition principle individual rays do not interact with each other. In a cavity with white walls we shall have thermodynamic equilibrium of rays of different temperature so that at each point there will exist at the same time several different temperatures. This equilibrium will not, however, be stable (see problem no. 93). If we give to rays the possibility to reduce to other rays, which is achieved by introducing in the cavity a speck of dust which radiates and absorbs light and has the role of mediator in the exchange of energy between frequencies, then radiation reduces to equilibrium radiation, becomes black and all rays have one and the same temperature.

Applied to radiation, thermodynamics enables us to establish the following:

- (1) the existence of radiation pressure (light pressure);
- (2) Kirchhoff's law which states that the ratio of the emissivity ϵ_ν to the absorptivity A_ν is independent of the nature of the substance;
- (3) Stefan-Boltzmann law of the temperature dependence of the total energy density of equilibrium radiation;

† The temperature of a black body that emits corresponding rays of a certain frequency is also called the temperature of these rays.

- (4) Wien's law on the spectral density of radiation;
- (5) the entropy increase in the reversible process of light refraction as a consequence of coherence of reflected ray and refracted ray.

Let us establish these results for equilibrium radiation.

1. *The existence of light pressure*

The presence of radiation pressure was firstly proved by Bartoli in 1876 on the basis of the second law of thermodynamics, by proceeding from the following imaginary experiment.

Let us consider two black bodies A and B having constant temperatures T_1 and T_2 ($T_1 > T_2$) joined to each other by means of a hollow

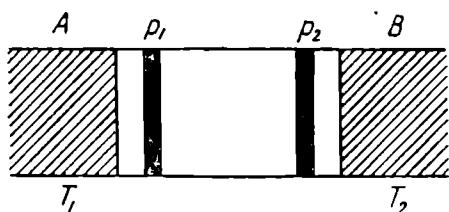


FIG. 20.

cylinder with white walls (Fig. 20). At the beginning and end of the cylinder there are slots for movable pistons having reflecting walls. Let us at first remove the piston P_2 from the cylinder, P_1 being left close to the surface of the body A . Thus the

volume of the cylinder will be filled with equilibrium radiation from the whole body B . Then, having inserted the piston P_2 and removed P_1 , we shall displace P_2 until it touches the body A ; then all the radiation in the cylinder will have been absorbed by the body A , and the cylinder is again filled with radiation from the body B .

Let us now insert the piston P_1 close to the surface of the body B and, after removing P_2 , let us displace P_1 up to the body A ; in the process all the energy radiated by B will again be absorbed by the body A .

By repeating this operation periodically we can transfer an arbitrary amount of radiant energy from the body B to the body A as a consequence of which the body A is heated and the body B is cooled, i.e. heat is transferred from a cold to a hot body. Since by the second law this can only occur at the expense of work, then in the case given the displacement of a piston must be accompanied by expenditure of work. Hence it follows that radiation produces pressure on the piston, this pressure being the larger the higher the radiation temperature.

Thermodynamics does not enable us to evaluate the magnitude of light pressure.† However, the light pressure p can easily be found by

† On the determination of the value of light pressure by thermodynamical means see problem no. 82.

proceeding from the laws of electrodynamics. If the energy density (i.e. the specific energy of equilibrium radiation) is equal to u then

$$p = \frac{u}{3}. \quad (5.48)$$

The presence of light pressure was firstly established experimentally in 1901 by P. N. Lebedev at the Physics Faculty of Moscow University.

2. Kirchhoff's law

Let two bodies be present in a closed cavity (Fig. 21): a black body A and a non-black body B . At equilibrium the temperatures of the bodies and radiation are the same, and the quantity of energy radiated during an arbitrary period of time by a unit surface of each body is equal to the quantity of energy absorbed by them during the same time.

Since the density of radiation energy in the cavity is everywhere the same, then on a unit surface of each body there is incident one and the same quantity of energy per second. Let this be equal to $I_\nu d\nu$. If the radiant emissivity of an absolute black body is equal to ε_ν^B then, at equilibrium, $I_\nu d\nu = \varepsilon_\nu^B d\nu$ and

$$\varepsilon_\nu^B = I_\nu. \quad (5.49)$$

A non-black body does not absorb all the incident energy $I_\nu d\nu$ but only a fraction of it, $A_\nu I_\nu d\nu$; at equilibrium $A_\nu I_\nu d\nu = \varepsilon_\nu d\nu$, whence, by taking (5.49) into account, we obtain

$$\frac{\varepsilon_\nu}{A_\nu} = \varepsilon_\nu^B = \text{const } (T, \nu). \quad (5.50)$$

This relation expresses *Kirchhoff's law*: the ratio of the radiant emissivity of a body to its absorptivity at a given temperature does not depend on the physical properties of the body and is equal to the radiant emissivity of the absolutely black body. The ratio ε_ν/A_ν is a universal function of temperature and frequency. As we shall see, thermodynamics does not enable us to find this function.

3. Stefan-Boltzmann law

Let us apply to equilibrium radiation the fundamental equation of thermodynamics

$$T dS = dU + p dV. \quad (3.32)$$

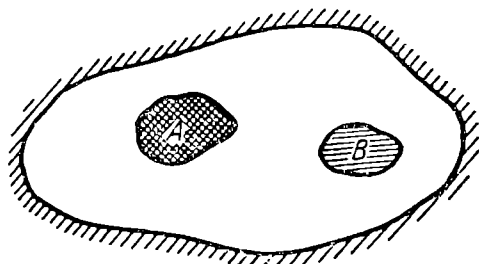


FIG. 21.

From this equation, by making use of the fact that dS is a total differential, we have obtained the relation (3.51)

$$T \left(\frac{\partial p}{\partial T} \right)_v = \left(\frac{\partial U}{\partial V} \right)_T + p. \quad (5.AL)$$

For equilibrium radiation $p = u/3$ and $U = uV$ and, accordingly, the equation (3.51) assumes the form

$$T \frac{du}{dT} = 4u. \quad (5.AM)$$

From this, after integrating, we obtain the temperature dependence of the total density of energy of equilibrium radiation

$$u = \sigma T^4, \quad (5.51)$$

which is called the *Stefan-Boltzmann law: the density of energy of equilibrium radiation is proportional to the fourth power of absolute temperature.*

Stefan established the law (5.51) in 1879 on the basis of experimental data, and Boltzmann obtained this law in 1884 by the method shown here on the basis of the second law of thermodynamics.

The integration constant σ (the constant of the Stefan-Boltzmann law) cannot be determined thermodynamically. Experiment, as well as statistical physics, give for σ the value

$$\sigma = 7.64 \times 10^{-15} \frac{\text{erg}}{\text{degree}^4 \text{ cm}^3} = 1.82 \times 10^{-22} \frac{\text{cal}}{\text{degree}^4 \text{ cm}^3}. \quad (5.AN)$$

By knowing the thermic equation of state of radiation (5.48) and its caloric equation of state $U = \sigma T^4 V$, we can evaluate the entropy of radiation

$$dS = \frac{\delta Q}{T} = \frac{dU + p dV}{T} = \frac{V du + (p + p) dV}{T} \quad (5.AO)$$

or

$$(5.AP)$$

$$dS = 4\sigma VT^2 dT + \frac{4}{3} \sigma T^3 dV = \frac{4}{3} \sigma (3VT^2 dT + T^3 dV) = d \left(\frac{4}{3} \sigma T^3 V \right)$$

and

$$S = \frac{4}{3} \sigma T^3 V. \quad (5.52)$$

The density of entropy of equilibrium radiation is equal to

$$s = \frac{4}{3} \sigma T^3. \quad (5.53)$$

The additive constant in (5.52) has been put equal to zero since for $u = 0$ the entropy must also vanish

$$(s = (4/3)(\sigma T^3) + s_0 = (4/3)(u/T) + s_0).$$

Since in an adiabatic process $S = \text{const}$, then by means of (5.32) we find the equation of an adiabatic of equilibrium radiation

$$VT^3 = \text{const}, \quad (5.54)$$

or

$$pV^{4/3} = \text{const}. \quad (5.55)$$

By comparing (5.55) with the equation of an adiabatic of an ideal gas (2.23) we observe that in adiabatic processes equilibrium radiation behaves like an ideal gas having a ratio of thermal capacities $\gamma = 4/3$. This, however, does not mean that in equilibrium radiation $\gamma = 4/3$. In equilibrium radiation $\gamma = \infty$ (see problem no. 86).

4. Wien's law

The Stefan-Boltzmann law gives an expression for the total energy density of equilibrium radiation but gives no information of its spectral composition. By considering radiation in a cavity (with a movable piston) (Fig. 22), the walls of which are ideally reflecting bodies, and applying to it the laws of thermodynamics and electrodynamics, Wien established in 1893 a new law which determines, though not completely, the spectral composition of equilibrium radiation. Let us find this law.



FIG. 22.

For a motion of the piston the temperature varies, as a consequence of the adiabaticity of the process, according to the law

$$VT^3 = \text{const}. \quad (5.54)$$

Also the frequency and energy of radiation vary in the reflection from the moving specular piston, since radiation accomplishes work on the piston in the process. The variations of these two quantities are easily obtained on the basis of the laws of thermodynamics and electrodynamics† and are determined by the relations

$$\frac{\nu}{T} = \text{const}, \quad (5.56)$$

$$\frac{u_\nu}{T^3} = \text{const}. \quad (5.57)$$

† See problem no. 85.

It follows from these relations that

$$\frac{u_\nu}{T^3} = \varphi\left(\frac{\nu}{T}\right), \quad u_\nu = T^3 \varphi\left(\frac{\nu}{T}\right) \quad (5. \text{AQ})$$

and

$$u_\nu = \nu^3 \cdot \frac{T^3}{\nu^3} \varphi\left(\frac{\nu}{T}\right) = \nu^3 f\left(\frac{\nu}{T}\right), \quad (5.58)$$

which is Wien's law. The form of the functions $\varphi(\nu/T)$ and $f(\nu/T)$ remains thermodynamically undetermined.

Wien's law leads to a determined shift of the maximum of the spectral density of radiation for a temperature variation. In fact, let us determine the frequency ν_m at which u_ν , equal to u_{ν_m} , is a maximum. To do this we differentiate (5.58) with respect to ν and equate the derivative to zero

$$3\nu_m^2 f\left(\frac{\nu_m}{T}\right) + \frac{\nu_m^3}{T} f'\left(\frac{\nu_m}{T}\right) = 0, \quad (5. \text{AR})$$

whence

$$\frac{\nu_m}{T} = \text{const} \quad (5. \text{AS})$$

or

$$\lambda_{\text{max}} \cdot T = b, \quad (5.59)$$

where b is Wien's constant.

Thus *the wavelength corresponding to a maximum of spectral density of the radiation energy of a black body is inversely proportional to temperature (Wien's displacement law)*. According to the latest measurements, Wien's constant is equal to $b = 0.288 \text{ cm}^\circ\text{K}$.

Wien's law (5.58) enables us from a given energy-distribution curve of the spectrum of black radiation at an arbitrary temperature T to plot the corresponding curve at any other temperature T_1 .

In fact, let the distribution curve for a temperature T be given. We shall find the corresponding curve for the temperature T_1 . Let us use the relation $\nu/T = \nu_1/T_1 = \text{const}$ (5.56). Then by Wien's formula

$$u_\nu(T_1, \nu_1) = \nu_1^3 f\left(\frac{\nu_1}{T_1}\right) = \left(\frac{T_1}{T}\right)^3 \nu^3 f\left(\frac{\nu}{T}\right) = \left(\frac{T_1}{T}\right)^3 u_\nu(T, \nu). \quad (5.60)$$

From this it can be seen that to construct the curve $u_\nu(T_1, \nu_1)$ from a given curve $u_\nu(T, \nu)$ we need to multiply the ordinate of each point of the given curve by the ratio $(T_1/T)^3$.

Wien's formula leads directly to the Stefan-Boltzmann law:

$$u = \int_0^{\infty} u_{\nu} d\nu = \int_0^{\infty} \nu^3 f\left(\frac{\nu}{T}\right) d\nu \quad (5.AT)$$

or, by introducing the new integration variable $\nu/T = x$ we shall obtain

$$u = T^4 \int_0^{\infty} x^3 f(x) dx = \sigma T^4. \quad (5.AU)$$

5. The non-additivity of the entropy of coherent rays

It can be seen from (5.60) that Wien's function $u_{\nu} = \nu^3 f(\nu/T)$ increases with a temperature increase if the wavelength remains constant. Therefore the function $f(x)$ is a decreasing function in the interval from $x = 0$ to $x = \infty$.

The fundamental equation of thermodynamics for the spectral densities of the energy and entropy of radiation gives

$$\frac{ds_{\nu}}{du_{\nu}} = \frac{1}{T}. \quad (5.AV)$$

Since T does not change its sign, then ds_{ν}/du_{ν} is always positive and decreases for an increase of u_{ν} , by varying in the interval from infinity to zero. Hence it follows that the function $s_{\nu}(u_{\nu})$ is a continuously

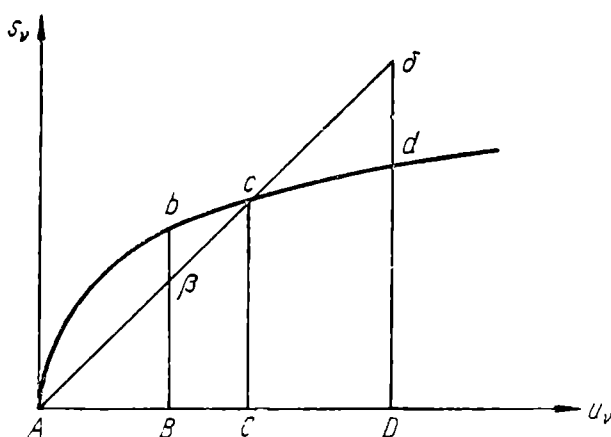


FIG. 23.

increasing and non-linear function of its argument. The graph of this function is similar to the curve shown in Fig. 23. For $u_{\nu} = 0$ the entropy s_{ν} is also equal to zero; therefore the curve passes through the

origin of the coordinates, has a vertical tangent at this point, is directed everywhere with its convexity upwards and assumes asymptotically a direction parallel to the axis of the abscissae.

All this leads us to conclude that the entropy of coherent rays is non-additive.

In fact, let a beam of rays of a determined frequency with specific energy u_ν be divided by means of a thin slab into two beams—a reflected and a refracted beam of specific energies $u_{\nu r}$ and $u_{\nu d}$ whereby

$$u_\nu = u_{\nu r} + u_{\nu d}, \quad (5. \text{AW})$$

since the energy remains unvaried. We shall denote the spectral densities of the entropies of both beams by $s_{\nu r}$ and $s_{\nu d}$ and shall prove that the total entropy has increased after the splitting of the beam into two, i.e. we shall prove that the following inequality is satisfied

$$s_\nu < s_{\nu r} + s_{\nu d}. \quad (5. \text{AX})$$

Let, in Fig. 23, $AB = u_{\nu r}$, $AC = u_{\nu d}$ and $AD = u_{\nu r} + u_{\nu d}$ so that $CD = AB$. Further let $Bb = s_{\nu r}$, $Cc = s_{\nu d}$ and $Dd = s_\nu$. If the function $s_\nu(u_\nu)$ were linear, then we would have the equality

$$Dd = Cc + Bb. \quad (5. \text{AY})$$

However, the function $s_\nu(u_\nu)$, as we have shown, is non-linear and is represented by the curve shown. Therefore the following inequality occurs

$$Dd < Cc + Bb, \quad (5. \text{AZ})$$

or

$$s_\nu < s_{\nu r} + s_{\nu d}. \quad (5.61)$$

From this the conclusion has been drawn that the process of decomposition of a beam is irreversible† though it can be completely reversed by means of mirrors.

This might seem a contradictory result. In reality, however, there is no contradiction. In fact, the conclusion of the irreversibility of the resolution of a beam is based on the assumption that the total entropy of the reflected and refracted beams can be obtained by adding the entropies $s_{\nu r}$ and $s_{\nu d}$. We have done just this in evaluating the total entropy of a system consisting of several parts (see the formula (5.45)). In the case just considered we must proceed differently. The fact is

† See problem no. 87.

that by employing the formula (5.45) we have assumed the separate monochromatic beams to be non-coherent, i.e. independent of each other. On the contrary a reflected beam is fully coherent with the refracted one since both originate from one and the same beam.

From the viewpoint of thermodynamics, to apply to two separate beams originating from the same source certain entropy-composition rules, and to beams of different origin other rules, is a new assumption which is beyond the scope of thermodynamics. This is quite natural since the coherence or incoherence of rays are not thermodynamic parameters.

Therefore, as soon as we turn to statistical thermodynamics which defines entropy according to Boltzmann's principle (3.39) in terms of the probability of a state, then our result (5.61) will become perfectly evident. In fact, only for two events independent of each other does the probability of their simultaneous occurrence equal the product of the probabilities, $W = W_1 W_2$, and therefore only for such phenomena

$$\ln W = \ln W_1 + \ln W_2 \quad (5.BA)$$

and

$$S = S_1 + S_2. \quad (5.BB)$$

If, however, events are not independent of each other and are connected by determined relations then $W \neq W_1 W_2$, and the entropy is non-additive $S \neq S_1 + S_2$, which is just what occurs in the case considered by us of coherent beams.

Having established Wien's law we have, in the first place, reached the limits of what thermodynamics can give. The result of the increasing of entropy in the reversible process of light refraction is already contradicting thermodynamics and points out its limitation. The latter is also indicated by the fact that it is impossible, within the limits of thermodynamics, to determine Kirchhoff's universal function or $f(\nu/T)$.

§ 27. Thermodynamics of plasma

A highly ionized gas the majority of the particles of which are electrically charged is called a plasma. Such a state of matter is encountered in stars, in the Earth's ionosphere, in gaseous discharge, in gases heated to a very high temperature, in a flame, in explosions etc.

In many respects plasma differs markedly from an ordinary gas. It shows in certain phenomena a similarity with electrolytes and solid conductors (metals, semiconductors) and possesses a number of specific properties. These distinctive features of plasma are mainly determined

by acting-at-a-distance electrical interaction forces between its particles. In fact, whereas in an ordinary gas the potential V_m of the intermolecular forces decays rapidly with the distance r (in the case of van-der-Waalsian attraction forces, $V_m \propto r^{-6}$) and moving particles interact appreciably with each other only during collisions, the potential V_e of interaction between plasma particles varies, according to Coulomb's law, inversely proportionally to the first power of distance $V_e \propto r^{-1}$, which leads to the interaction of particles also at large distances (and therefore to prolonged interaction).

A great part of our knowledge of plasma has been obtained from investigations of gaseous discharge. Interest in the study of plasma has increased markedly in our time in connexion with the utilization, for the purpose of obtaining energy, of the thermonuclear reactions of the synthesis of light nuclei. At a high gas temperature, when the gas is found in a state of plasma and particles move with great velocities, Coulomb's potential barrier can be overcome in the collisions of atom nuclei and their synthesis is possible. Of especially great importance in practice is the excitation of thermonuclear reactions in deuterium, since in this case such reactions can occur at relatively lower temperatures ($T \approx 10^6$ °K). The "burning" of nuclei of deuterium as a result of their synthesis into α -particles leads to the release of a large quantity of energy.

We shall consider plasma in thermodynamic equilibrium, consisting of two kinds of oppositely charged particles (e and $-e$). In order to reach a high degree of ionization, we need first of all to reduce as much as possible the recombination rate of particles. This is possible at low pressures, since the recombination coefficient is proportional to pressure. The mean Coulombian interaction energy between two particles e^2/\bar{r} (\bar{r} is the mean distance between the particles) is small in this case in comparison with the energy kT of thermal motion of the particles. The inequality

$$\frac{e^2}{\bar{r}} < kT \quad (5.BC)$$

expresses the condition of rarefaction of plasma. In order to obtain a fully ionized plasma we need to heat the gas to such a temperature T that the mean energy of thermal motion of an atom be equal to or larger than its ionization potential I .

$kT \geq I$ (the condition of complete ionization):

In the case of hydrogen or deuterium the ionization potential is equal

to 13.54 eV ($1 \text{ eV} = 1.6 \times 10^{-12} \text{ erg}$), and therefore fully ionized hydrogen plasma will be obtained at temperatures

$$T \geq \frac{I}{k} = \frac{13.54 \times 1.6 \times 10^{-12}}{1.38 \times 10^{-16}} \approx 160,000^\circ \text{K}. \quad (5.BD)$$

At such high temperatures plasma can no longer be considered as a system consisting of only charged particles; we need to take into account also the radiation contained in it. In investigating the thermodynamic properties of systems up to 1000°K we do not always take into account the radiation existing in them, since its energy is very small in comparison with the internal energy of thermal motion of the particles of the system. Such an approach would be incorrect at very high temperature. We can easily find the temperature at which the energy density of radiation σT^4 will become equal to the energy density of thermal motion of the particle $3kTn/2$ (n is the number of particles per unit volume)

$$\sigma T^4 = \frac{3}{2} kTn \quad (5.BE)$$

and

$$T = \sqrt[3]{\frac{3kn}{2\sigma}}. \quad (5.BF)$$

At a gas pressure $p = 0.01 \text{ mm Hg}$, when the density of particles $n \approx 10^{15} \text{ cm}^{-3}$, this temperature is $T \approx 4 \times 10^4^\circ \text{K}$.

Thus at temperatures of complete plasma ionization ($T \approx 10^5^\circ \text{K}$) the energy density of the radiation in it becomes predominant. This leads to a very important consequence, which is undesirable in practice in thermonuclear reactions, namely the difficulty of adiabatically insulating such plasma.

In order to determine the thermodynamic properties of plasma we shall find, as a thermodynamic potential, its free energy at not too high temperatures when the free energy of radiation can be neglected. The taking of the latter into account does not involve difficulties and it can easily be done if the plasma temperature is of the order of 10^5°K .

The internal energy of plasma, U , is made up of the kinetic energy of random motion of its particles U_{id} (the internal energy of an ideal gas) and the mean energy of their electrostatic interaction U_e

$$U = U_{id} + U_e. \quad (5.BG)$$

Neither U_{id} nor U_e can be evaluated in thermodynamics but are taken from experiment or are found by methods of statistical physics. The

value of U_{id} is known to us (see problem no. 9): $U_{id} = C_v T + U_0$. The expression for U_e (the derivation of which is shown in the solution of the problem no. 76) has the form

$$U_e = -\frac{e^2}{d} N, \quad (5.BH)$$

where e is the charge of the particles, N is the number of the particles of one kind in the volume V , and $d = (kTV/8\pi Ne^2)^{1/2}$ is Debye's radius which determines the penetration depth of an external electrical field into plasma. The negative value of U_e is due to the prevailing of attraction forces in the plasma since each charge is surrounded by a cloud of charges of opposite sign.

Thus the internal energy of plasma is equal to

$$U = U_{id} - Ne^2 \sqrt{\frac{8\pi Ne^2}{kTV}}. \quad (5.BJ)$$

This expression for U is not, however, a thermodynamic potential. Therefore, to obtain a thermodynamic potential, we shall determine the free energy $F(T, V)$ by integrating the Gibbs-Helmholtz equation $U = F - T(\partial F/\partial T)_v$:

$$U = F - T \left(\frac{\partial F}{\partial T} \right)_v = -T^2 \frac{\partial}{\partial T} \left(\frac{F}{T} \right), \quad (5.BK)$$

whence

$$F = -T \int \frac{U}{T^2} dT + IT, \quad (5.BL)$$

which in our case gives

$$F = F_0 - \frac{2}{3} Ne^2 \sqrt{\frac{8\pi Ne^2}{kTV}}. \quad (5.BM)$$

Since at a high degree of rarefaction ($V \rightarrow \infty$ for a given N) the free energy of plasma becomes equal to the free energy of an ideal gas F_{id} , then it follows that $F_0 = F_{id}$ and

$$F = F_{id} - \frac{2}{3} Ne^2 \sqrt{\frac{8\pi Ne^2}{kTV}}. \quad (5.BN)$$

The thermic equation of state of plasma, its entropy and thermal capacity can now be determined by means of the expressions

$$p = -\left(\frac{\partial F}{\partial V} \right)_T, \quad S = -\left(\frac{\partial F}{\partial T} \right)_v, \quad C_v = -T \left(\frac{\partial^2 F}{\partial T^2} \right)_v. \quad (5.BO)$$

As a result we obtain

$$\left. \begin{aligned} p &= \frac{RT}{V} - \frac{1}{3} Ne^2 \sqrt{\frac{8\pi Ne^2}{kTV^3}}, \\ S &= (C_v)_{id} \ln T + R \ln V - \frac{1}{3} Ne^2 \sqrt{\frac{8\pi Ne^2}{kT^3V}}, \\ C_v &= (C_v)_{id} + \frac{1}{2} Ne^2 \sqrt{\frac{8\pi Ne^2}{kT^3V}}. \end{aligned} \right\} \quad (5. BP)$$

The pressure and entropy of plasma is less than in an ideal gas, which is explained by the prevailing in it of attraction forces. On the other hand the thermal capacity of plasma is larger than the thermal capacity of an ideal gas, which is also physically evident: in increasing the temperature of plasma we have to expend energy not only for increasing the kinetic energy of the random motion of its particles, but also for increasing the mean potential energy of interaction between particles as a consequence of the variation of the cloud of oppositely charged particles about each particle.

§ 28. The thermodynamics of systems with a variable number of particles

Let us find expressions for the differentials of the thermodynamic potentials of systems with a variable number of particles.

A variation in the number of particles of a system can arise from various causes. For example, in the case of a system consisting of liquid and its saturated vapour, particles from the liquid pass to the vapour phase and vice versa. In this connexion the total number of particles in the two phases remains constant, but the number in each phase varies. A variation of the number of particles in a system occurs in chemical reactions when the number of particles of some kind or other is a variable quantity. A third example of a system with a variable number of particles is radiation. Equilibrium radiation is a set of quantum-indistinguishable particles, photons, which in contrast to ordinary classical particles exhibit both corpuscular and wave properties. In the absorption and radiation of light by walls the number of these particles is varying all the time.

Again and again, in the study of systems of elementary particles, modern physics establishes the presence in nature of processes in which not only the number of particles of a determined kind but also the total

number of particles varies as a result of their mutual transformation in the system.

The state of a system with a variable number of particles is characterized by the parameters T, a_1, a_2, \dots, a_n and by the number of particles of a given kind N_1, \dots, N_r, \dots or their corresponding concentrations $c_i = N_i/\Sigma N_i$.

The internal energy of a system with a variable number of particles varies not only owing to heat communicated to and work accomplished by the system, but also owing to variation of the number of particles in the system, and therefore by the first law of thermodynamics we have

$$dU = \delta Q - \delta W + \sum_k \mu_k dN_k \quad (5.62)$$

(k determines the kind of particles the number of which varies in the system). In quasi-static processes

$$\delta Q = T dS \quad \text{and} \quad \delta W = \sum_i A_i da_i, \quad (5.BQ)$$

and therefore the fundamental equation of thermodynamics for systems with a variable number of particles for quasi-static processes in such systems assumes the form

$$T dS = dU + \sum_i A_i da_i - \sum_k \mu_k dN_k, \quad (5.63)$$

and for non-static processes, similarly to (3.49):

$$T dS > dU + \sum_i A_i da_i - \sum_k \mu_k dN_k. \quad (5.63')$$

The quantity

$$\mu_k = \left(\frac{\partial U}{\partial N_k} \right)_{S, a_i} \quad (5.BR)$$

is called the *chemical potential* of the k -th kind of particles.

By means of the fundamental equation (5.63) it is easy to obtain the differentials for all thermodynamic potentials of systems with a variable number of particles. To make matters simpler we shall consider systems that are subject to the action of only uniform pressure p . For the differential of the internal energy of such a system we have

$$dU = T dS - p dV + \sum_i \mu_i dN_i, \quad (5.64)$$

for the free energy $F = U - TS$ we have

$$dF = dU - T dS - S dT = -S dT - p dV + \sum_i \mu_i dN_i, \quad (5.65)$$

similarly for Gibbs' thermodynamic potential $Z = U - TS + pV$

$$dZ = -S dT + V dp + \sum \mu_i dN_i \quad (5.66)$$

and for the enthalpy $H = U + pV$ we have

$$dH = T dS + V dp + \sum \mu_i dN_i. \quad (5.67)$$

From these expressions the chemical potential is evidently equal to

$$\mu_i = \left(\frac{\partial U}{\partial N_i} \right)_{S, V} = \left(\frac{\partial F}{\partial N_i} \right)_{T, V} = \left(\frac{\partial Z}{\partial N_i} \right)_{T, p} = \left(\frac{\partial H}{\partial N_i} \right)_{S, p}. \quad (5.68)$$

Thus μ can be obtained by differentiating any one of the thermodynamic potentials with respect to the number of particles, but the expressions obtained will be in terms of different variables.

As has already been observed, all thermodynamic potentials are additive functions, i.e. their values for a set of several bodies are equal to the sum of their values for each body. In the case of a system consisting of equal particles this means that when the quantity of the substance, i.e. the number of particles, N , varies in a certain ratio the value of such functions varies in the same ratio. In other words it can be said that an additive thermodynamic quantity must be a homogeneous function of the first order with respect to additive variables. Therefore:

$$\left. \begin{aligned} U &= N f_1 \left(\frac{S}{N}, \frac{V}{N} \right), \\ F &= N f_2 \left(T, \frac{V}{N} \right), \\ Z &= N f_3 (T, p), \\ H &= N f_4 \left(\frac{S}{N}, p \right), \end{aligned} \right\} \quad (5.69)$$

and in the case of a system comprising various kinds of particles:

$$\left. \begin{aligned} U &= \sum N_i f \left(\frac{S_i}{N_i}, \frac{V_i}{N_i}, c_i \right), \\ Z &= \sum N_i f (T, p, c_i), \end{aligned} \right\} \quad (5.70)$$

where V_i is the volume occupied by particles of the i -th kind and c_i is the concentration of this kind of particles.

From (5.70)

$$\mu_i = \left(\frac{\partial Z}{\partial N_i} \right) = f(T, p, c_i), \quad (5.71)$$

i.e. the chemical potential is equal to the thermodynamic potential per one particle, and therefore

$$Z = \sum \mu_i N_i. \quad (5.72)$$

However, neither U , nor F , nor H are equal to sums of this type

$$U \neq \sum \mu_i N_i, \quad F \neq \sum \mu_i N_i, \quad H \neq \sum \mu_i N_i. \quad (5.BS)$$

As can be seen from (5.71), the chemical potential is a function of T , p and c_i but does not depend on the total number of particles N_i .

For equilibrium radiation $\mu = 0$ (see problem no. 88) which, as is shown by statistical physics, corresponds to the fact that the total number of particles in the system is not assigned but depends on temperature.

PROBLEMS

78. The temperature dependence of the e.m.f. of a certain cell is given by the formula

$$\mathcal{E} = 0.96466 + 1.74 (t^\circ - 25) \cdot 10^{-4} + 3.8 (t^\circ - 25)^2 \times 10^{-7} \text{ v}. \quad (5.BT)$$

Determine the fraction of the e.m.f. of the cell which is supplied by the heat reservoir and the value of the reaction heat at 25 °C.

79. Find the dependence of the electromotive force of a reversible galvanic cell on the external pressure.

80. The Joule-Thomson process is irreversible. Is this irreversibility taken into account in finding the coefficient μ determined by the equality (5.7)?

81. If the density of a gas is small then (5.10) leads to the inversion temperature (5.11). Show that for large densities there are two inversion points.

82. In some textbooks of thermodynamics the following proof is shown for obtaining the value of the pressure of radiation incident normally on a black surface.

Let light energy of density u be normally incident on a unit surface of a still black body; then in a unit time interval on a unit surface of the body there arrives a quantity of energy uc , where c is the velocity of light, and the quantity of light arriving during the time dt is equal to $ucdt$. This energy is absorbed by the body and is transformed in it into a quantity of heat $\delta Q = uc dt$. Let, further, a body be displaced under the action of light pressure during the time dt in the direction of the light beam with velocity v ; then the quantity of light energy arriving on a unit surface of the body during the time dt (and therefore also the quantity of heat acquired by the body) must be $\delta Q_1 = u(c - v) dt$. This quantity of heat is smaller than the previous one by the value $uvdt = udx$, where dx is the displacement of the body under the action of light pressure during the time dt .

Further, the quantity of energy radiated by the source during one and the same time must be the same in both cases; in the first case all the energy during the time dt is transformed into the heat δQ , and in the second case the same quantity of energy is partly transformed into the heat δQ_1 and partly into the work of displacement of the body pdx , where p is light pressure. Hence $\delta Q - \delta Q_1 = pdx$, and since this difference of heats absorbed is equal by the above considerations to udx then it follows that

$$p = u. \quad (5.BU)$$

Point out the error in the above proof of the value of light pressure.

83. Evaluate the thermodynamic potentials U , F , Z and H for equilibrium radiation.

84. Show that in an adiabatic process black radiation remains black but varies its temperature.

85. Show that in an adiabatic expansion of equilibrium radiation the variations of its frequency and spectral energy density are determined by the relations

$$\frac{\nu}{T} = \text{const} \quad \text{and} \quad \frac{u_\nu}{T^3} = \text{const}. \quad (5. BV)$$

86. Determine c_V , c_p , $c_p - c_V$ and c_p/c_V for a unit volume of equilibrium radiation. Compare c_V for a unit volume of a monatomic gas with c_V of the equilibrium radiation contained in it.

87. The entropy of radiation increases when a beam of light is divided into a reflected and a refracted beam. From this it has been incorrectly concluded that the process of reflection and refraction of light is irreversible. Show other methods of establishing this result.

88. Evaluate the chemical potential of an ideal gas and equilibrium radiation.

89. Determine which function is a thermodynamic potential in terms of the independent variables T , V and μ .

CHAPTER VI

CONDITIONS OF THERMODYNAMIC EQUILIBRIUM AND THEIR APPLICATION

By extending to thermodynamic systems the mechanical principle of virtual displacements, Gibbs developed the theory of thermodynamic equilibrium.

Before we proceed to establish (following Gibbs) equilibrium conditions, we shall consider at first a classification of thermodynamic systems.

§ 29. Homogeneous and heterogeneous systems.

Phases and components

All thermodynamic systems can be attributed to one of two large classes: homogeneous and heterogeneous systems.

Homogeneous systems are those in which the properties vary continuously in moving from one of their points to another. Usually homogeneous systems are identified with physically homogeneous systems, i.e. with such ones as have equal physical properties in any arbitrarily chosen parts of equal volume. Examples of such systems are mixtures of various gases and either liquid or solid solutions. In such systems reactions can occur between the component parts of a mixture, the dissociation of a gas or of a dissolved substance, polymerization (i.e. the formation from simpler molecules of more complex ones, for example the formation of a single molecule of $(C_2H_4O)_3$ from three molecules of C_2H_4O , or of a single more complex water molecule $(H_2O)_2$ from two water molecules H_2O etc.) and solvation (i.e. the orientation of molecules of solvent about an ion or other particle of a dissolved substance). Under equilibrium conditions reactions in such systems apparently cease. The laws of systems in equilibrium are established by means of the laws of thermodynamics.

Heterogeneous systems are defined as those systems that consist of several physically homogeneous bodies, so that inside them there are

discontinuities in the variation of their properties. Such systems can be either various states of aggregation of one and the same substance (ice–water, water–vapour etc.) or various crystal modifications (grey and white tin), or various products of mutual solution (the aqueous solution of a salt—the solid salt—the vapour), or products of the chemical interaction of various substances (liqui dalloy and solid chemical combination of two metals).

A physically homogeneous body that is part of a heterogeneous system and is separated from other parts by a separation surface on which some properties (and the parameters corresponding to them) vary with a jump, is called a *phase*. If a system consists of liquid and vapour, then the liquid represents a phase and the vapour another phase. States of aggregation should not be confused or identified with phases. Whereas there are only three states of aggregation: the solid, liquid and gaseous states, there are an unlimited number of phases; even in one and the same chemically pure substance in the solid state of aggregation there can exist several phases (rhombic and monoclinic sulphur, grey and white tin etc.). At small pressures when gases do not differ markedly from ideal gases, only one phase can exist in the gaseous state, since under such conditions all gases are capable of mixing, with each other in any proportions and form a homogeneous system.† In the liquid state, several phases can coexist in equilibrium, for example water and oil, kerosene and water etc.

In addition to the concept of phase, the concept of component has great importance in investigations of the equilibrium of thermodynamic systems (both heterogeneous and homogeneous systems). A *component* is such a part of a system the contents of which do not depend on the contents of other parts. A mixture of gases is a single-phase but multi-component system: in a mixture of chemically non-reacting gases there are as many components as there are different gases. Water (or ice) is also a single-phase system but has one component only, since hydrogen and oxygen occur in it in a well-determined ratio: the quantity of one of them does depend on the quantity of the other. Thus, in general, if in a phase there are N different substances (chemical elements) among which there exist n chemical reactions the number of components (the number of independent substances in such a phase) will be $N-n$.

† On the limits of the mutual solubility of gases at high pressures see: I. R. Krichevskii; *Fazovye ravnovesiya v rastvorakh pri vysokikh davleniyakh* (Phase Equilibria in Solutions at High Pressures), Goskhimizdat, 1946.

A system with two components is called a binary system (a mixture of two gases, a mixture of two liquids or a mixture of two solids etc.), a system with three components is called a ternary system etc.

§ 30. General conditions of thermodynamic equilibrium

The fundamental equation of thermodynamics for non-static processes enables us to establish general sufficient conditions for the equilibrium of thermodynamic systems. By assuming, in accordance with experiment, the existence of fluctuations in [all] systems (and therefore by exceeding the limits of the initial propositions of thermodynamics) these conditions can be shown to be also necessary.

As has already been pointed out, the theory of thermodynamic equilibrium was developed by Gibbs on the model of Lagrange's analytical mechanics [lit. mechanical statics], i.e. by extending the principle of virtual displacements in mechanics.

It is known from mechanics that under ideal constraints a mechanical system is found to be in equilibrium if the sum of the works of all applied forces is equal to zero for an arbitrary virtual displacement of the system (the principle of virtual displacements). By describing this principle—the general equilibrium condition—in the language of analysis in the form of an equation, and solving this simultaneously with the equations determining the virtual displacements, concrete equilibrium conditions can be found for a mechanical system in each given problem. The equations satisfied by virtual displacements and the equation of the principle of virtual displacements are written down in the following manner.

Let the state of a mechanical system be determined by the coordinates q_1, q_2, \dots, q_n and let the constraints imposed on the system be expressed by the conditions

$$f_s(q_1, q_2, \dots, q_n) = 0 \quad (s = 1, 2, \dots, k \leq n). \quad (6.A)$$

Then the displacements $\delta q_1, \delta q_2, \dots, \delta q_n$ that are compatible with these constraints and which are called virtual or possible displacements satisfy, evidently, the equations

$$\sum_{i=1}^n \frac{\partial f_s}{\partial q_i} \delta q_i = 0. \quad (6.1)$$

If the generalized force associated with the coordinate q_i is Q_i then the principle of virtual displacements will be written in the form

$$\sum_{i=1}^n Q_i \delta q_i = 0. \quad (6.2)$$

By solving the equations (6.1) and (6.2) simultaneously by the method of Lagrange's indeterminate factors, concrete equilibrium conditions are obtained for a given mechanical system.

Let us extend this method of determining equilibrium conditions to thermodynamic systems.

The state of equilibrium of a thermodynamic system is determined by the temperature T and by the external parameters a_1, a_2, \dots, a_n , characterizing the relation of the system with external bodies.

According to the second initial proposition of thermodynamics, all internal parameters are functions, at equilibrium, of external parameters and temperature, and therefore they are not needed for determining the state of equilibrium of the system. If the system departs from its state of equilibrium, the internal parameters are no longer functions of the external parameters and temperature; therefore a non-equilibrium state needs to be characterized by additional independent parameters. This enables us to consider a non-equilibrium system as one in equilibrium but having a larger number of parameters and generalized forces, associated with them, which "hold" the system in equilibrium, the thermodynamic functions of the system in the non-equilibrium state being assumed to be equal to the values of these functions when the system is at equilibrium with the additional "holding" forces.†

On the basis of this notion, by considering the departure of a system from a state of equilibrium as the result of virtual deviations of internal parameters from their equilibrium values, we can, by using the fundamental equation of thermodynamics (3.49), obtain general equilibrium conditions of thermodynamic systems. In this connexion, since the state of thermodynamic systems is determined not only by mechanical parameters but also by specifically thermodynamic parameters (temperature, entropy etc.) and other parameters, then, instead of the single general equilibrium condition for mechanical systems (6.2), there will

† The role of such forces is performed by external fields and adiabatic diaphragms, separating a part of the system from another if the temperature of these parts is different.

be for thermodynamic systems several equilibrium conditions, depending on the relation of the system with external bodies (whether the system is adiabatic, isothermal etc.).

By solving in each such case the general equilibrium condition of the system simultaneously with the equations for the virtual variations of external parameters, we can obtain the concrete equilibrium conditions of thermodynamic systems in this case.

Equations for the virtual variations of external parameters are found similarly to (6.1). Let the system have m internal parameters b_1, b_2, \dots, b_m which assume, in equilibrium, the values $b_1^\circ, b_2^\circ, \dots, b_m^\circ$. These parameters are, generally speaking, connected by conditions of the form

$$f_s(b_1, b_2, \dots, b_m) = 0 \quad (s = 1, 2, \dots, k \leq m). \quad (6.B)$$

Variations of internal parameters that are compatible with these constraints, i.e. virtual variations, satisfy, evidently, the equations

$$\sum_{i=1}^m \frac{\partial f_s}{\partial b_i} \delta b_i = 0. \quad (6.3)$$

We shall now obtain general equilibrium conditions of a system in various cases.

1. *An isolated system* ($U = \text{const}, V = \text{const}$)

The fundamental equation of thermodynamics for non-static processes

$$T dS > dU + p dV \quad (6.4)$$

for $U = \text{const}$ and $V = \text{const}$ gives

$$dS > 0, \quad (6.C)$$

i.e. *the entropy of an isolated system increases for non-static processes*. When these processes cease and equilibrium occurs, the entropy of the system will evidently be a maximum.

Thus the *general equilibrium condition of an isolated system is that its entropy must be a maximum*. By denoting the entropy of a system in a non-equilibrium state by S , the equilibrium entropy by S° and the difference $S - S^\circ$ by ΔS , we can write the general equilibrium condition of an isolated system as the maximum-entropy condition in the form

$$\Delta S < 0 \quad \text{or} \quad \delta S = 0, \quad \delta^2 S < 0, \quad (6.5)$$

i.e. the first order variation of entropy is equal to zero and the second is negative. This condition is sufficient since, if a system having maxi-

num entropy were not in equilibrium, then in approaching it the system entropy would begin to increase which would contradict the hypothesis of its being a maximum. We cannot, on the basis of the fundamental equation (6.4), prove that the maximum-entropy condition is a necessary condition for an isolated system, since it does not follow from (6.4) that equilibrium is impossible for non-maximum entropy. However, by bearing in mind the molecular nature of thermodynamic systems and the presence, caused by it, of fluctuations of the internal parameters, we see that an equilibrium state without an entropy maximum is impossible since, owing to these fluctuations, non-static processes arise in the system that are accompanied by an increase of entropy and lead the system to equilibrium with maximum entropy.

Thus the presence of fluctuations in systems leads to the necessity for a maximum of entropy at equilibrium, and therefore whenever this condition is not fulfilled the system is not found in equilibrium.

As an example we shall consider the equilibrium of a two-phase system of one and the same substance (for example, water and its vapour) and, by proceeding from the general equilibrium condition (6.5) we shall find concrete equilibrium conditions of such a system.

The entropy of the system is equal to

$$S = N_1 s_1 + N_2 s_2, \quad (6.6)$$

where N_1 and N_2 are the numbers of molecules in the first and second phase, and s_1 and s_2 are the entropies for a single molecule of these phases. For an isolated system we have

$$\left. \begin{aligned} N_1 + N_2 &= N = \text{const} \text{ — the total number of particles,} \\ N_1 u_1 + N_2 u_2 &= U = \text{const} \text{ — the total internal energy of} \\ &\quad \text{the system,} \\ N_1 v_1 + N_2 v_2 &= V = \text{const} \text{ — the volume of the whole} \\ &\quad \text{system.} \end{aligned} \right\} \quad (6.7)$$

As the independent external parameters of the system we shall take the quantities N_1 , v_1 and u_1 ; the dependent variables will be N_2 , v_2 and u_2 .

We shall solve simultaneously the equilibrium-condition equation

$$\delta S = 0 \quad (6.D)$$

with the equations determining the virtual variations of the internal parameters

$$\delta N = 0, \quad \delta U = 0, \quad \delta V = 0. \quad (6.E)$$

From (6.6) we have

$$\delta S = N_1 \delta s_1 + N_2 \delta s_2 + s_1 \delta N_1 + s_2 \delta N_2 = 0. \quad (6.8)$$

From (6.7) we have

$$\left. \begin{aligned} \delta N &= \delta N_1 + \delta N_2 = 0, \\ \delta U &= N_1 \delta u_1 + u_1 \delta N_1 + N_2 \delta u_2 + u_2 \delta N_2 = 0, \\ \delta V &= N_1 \delta v_1 + v_1 \delta N_1 + N_2 \delta v_2 + v_2 \delta N_2 = 0. \end{aligned} \right\} \quad (6.9)$$

The equation (6.8) can be written in the form

$$N_1 \frac{\delta u_1 + p_1 \delta v_1}{T_1} + N_2 \frac{\delta u_2 + p_2 \delta v_2}{T_2} + s_1 \delta N_1 + s_2 \delta N_2 = 0. \quad (6.F)$$

By substituting in here the values found from (6.9)

$$\begin{aligned} \delta N_2 &= -\delta N_1, \\ N_2 \delta u_2 &= -N_1 \delta u_1 + (u_2 - u_1) \delta N_1, \\ N_2 \delta v_2 &= -N_1 \delta v_1 + (v_2 - v_1) \delta N_1, \end{aligned} \quad (6.G)$$

we shall obtain

$$\begin{aligned} N_1 \frac{\delta u_1 + p_1 \delta v_1}{T_1} + \frac{-N_1 \delta u_1 + (u_2 - u_1) \delta N_1 + p_2 [-N_1 \delta v_1 + (v_2 - v_1) \delta N_1]}{T_2} + \\ + s_1 \delta N_1 - s_2 \delta N_1 = 0, \end{aligned} \quad (6.H)$$

or

$$\begin{aligned} N_1 \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \delta u_1 + N_1 \left(\frac{p_1}{T_1} - \frac{p_2}{T_2} \right) \delta v_1 + \\ + \left[\left(s_1 - \frac{u_1 + p_1 v_1}{T_2} \right) - \left(s_2 - \frac{u_2 + p_2 v_2}{T_2} \right) \right] \delta N_1 = 0. \end{aligned} \quad (6.J)$$

Since the variations δN_1 , δv_1 and δu_1 are independent, we obtain finally the following equilibrium conditions of two phases of one and the same substance:

(a) $(1/T_1) - (1/T_2) = 0$ and $T_1 = T_2 = T$, the equality of the temperatures (the condition of thermal equilibrium);

(b) $(p_1/T) - (p_2/T) = 0$ and $p_1 = p_2 = p$, the equality of the pressures in the phases (the condition of mechanical equilibrium);

(c) $s_1 - (u_1 + p v_1)/T = s_2 - (u_2 + p v_2)/T$ and $u_1 - T s_1 + p v_1 = u_2 - T s_2 + p v_2$, or $\mu_1 = \mu_2$, the equality of the chemical potentials of the two phases (the condition of chemical equilibrium).

2. *A system in a thermostat of constant volume* ($T = \text{const}$, $V = \text{const}$)

The fundamental equation of thermodynamics for non-static processes (6.4) expressed in terms of the independent variables T and V assumes the form

$$dF < -S dT - p dV. \quad (6.10)$$

For a system in a thermostat, if the system does not accomplish work, we have

$$dF < 0, \quad (6.K)$$

i.e. in an isothermal system the free energy decreases in non-static processes and is a minimum at equilibrium. This general equilibrium condition of an isothermal system not accomplishing external work can be written in the form

$$\Delta F > 0 \quad \text{or} \quad \delta F = 0, \quad \delta^2 F > 0. \quad (6.11)$$

3. *A system in a thermostat under constant external pressure* ($T = \text{const}$, $p = \text{const}$).

The fundamental equation of thermodynamics (6.4), expressed in terms of the variables T and p , assumes the form

$$dZ < S dT - V dp. \quad (6.12)$$

For a system immersed in a medium of constant temperature and pressure we obtain

$$dZ < 0, \quad (6.L)$$

i.e. in such a system the thermodynamic potential decreases in non-static processes and has a minimum at equilibrium. Therefore the general equilibrium condition of a system in a thermostat at constant external pressure—a minimum of Gibbs' thermodynamic potential—is written in the form

$$\Delta Z > 0 \quad \text{or} \quad \delta Z = 0, \quad \delta^2 Z > 0. \quad (6.13)$$

It can be shown in a similar manner† that in a system with constant entropy and pressure, equilibrium occurs for a minimum of enthalpy

$$\Delta H > 0 \quad \text{or} \quad \delta H = 0, \quad \delta^2 H > 0, \quad (6.14)$$

while in a system with constant entropy and volume equilibrium occurs for a minimum of internal energy

$$\Delta U > 0 \quad \text{or} \quad \delta U = 0, \quad \delta^2 U > 0. \quad (6.15)$$

† See problem no. 92.

4. *A system with a variable number of particles in a thermostat* ($T = \text{const}$, $p = \text{const}$, $\mu_i = \text{const}$)

Let us express the fundamental equation of thermodynamics for a system with a variable number of particles

$$T dS \geq dU + p dV - \sum_i \mu_i dN_i \quad (5.33)$$

in terms of the variables T , p and μ_i . To do this we shall add to both sides of (5.33) the differential $d(U - TS + pV - \sum_i \mu_i N_i)$. Then we shall obtain

$$d(U - TS + pV - \sum_i \mu_i N_i) \leq V dp - S dT - \sum_i N_i d\mu_i \quad (6.16)$$

or

$$dB \leq V dp - S dT - \sum_i N_i d\mu_i, \quad (6.17)$$

where

$$B = U - TS + pV - \sum_i \mu_i N_i. \quad (6.18)$$

It can be seen from (6.16) that in a system with a variable number of particles that is found in a thermostat at constant values of p and μ_i , the thermodynamic potential B decreases in non-static processes ($dB < 0$) and has a minimum equal to zero† at equilibrium. The general equilibrium condition of such a system will be written in the form

$$\Delta B > 0 \quad \text{or} \quad \delta B = 0, \quad \delta^2 B > 0. \quad (6.19)$$

Thus general equilibrium conditions of thermodynamic systems under various conditions are determined by extremum values of corresponding thermodynamic potentials. These conditions are not only sufficient but also necessary if all other conditions for the establishing of equilibrium are ensured (since the conditions found by us are not the only ones needed for the processes to take place‡).

Thermodynamic potentials can have several extrema (entropy can have a number of maxima). States corresponding to the largest of them (in the case of entropy) or to the smallest of them (in the case of free energy and other thermodynamic potentials) are called *stable* (*abso-*

† See § 31.

‡ In certain cases processes are thermodynamically possible (the thermodynamic potentials vary with them in accordance with the conditions found), but they do not in reality take place since other conditions are not fulfilled (for example, certain chemical reactions take place only in the presence of catalysts, although they are always possible thermodynamically in that the free energy decreases for their occurrence).

lutely stable equilibrium states), and the others are called *metastable* (or *semistable*). In the presence of large fluctuations a system can pass from a metastable to a stable state.

§ 31. Stability conditions for the equilibrium of a homogeneous system

The general equilibrium conditions of thermodynamic systems are expressed by the extremum behaviour of thermodynamic potentials. Thus in the case of an isolated system the equilibrium condition is a maximum value of entropy, which is expressed by the inequality $\Delta S < 0$ or by the two relations $\delta S = 0$ and $\delta^2 S < 0$. In determining concrete equilibrium conditions of two phases of an arbitrary substance we have used only the first relation ($\delta S = 0$). However, the equality to zero of the first variation is only a necessary condition for [the existence] of an extremum and does not ensure that the entropy will be just a maximum. A sufficient condition for a maximum of entropy is the negative value of its second variation, which also ensures stability of equilibrium. If, however, for $\delta S = 0$ the second variation of entropy is positive (a minimum of entropy) then the corresponding state of the system will be an equilibrium state but absolutely unstable,† since owing to the presence of fluctuations in it non-static processes will be started that will lead the system to an equilibrium state with a maximum of entropy. Then, since entropy cannot increase further, this equilibrium will be stable.

The same can also be said of a system with a variable number of particles in a thermostat for given values of p and μ_i . In this case the conditions of equilibrium stability of the system are determined by the inequality $\Delta B > 0$ or $\delta^2 B > 0$.

Let us find concrete equilibrium-stability conditions of such homogeneous systems.

We shall take as an example of parameters (coordinates) of the system the entropy S , the volume V and the number of particles N_i of various kinds. For assigned values of T , p and μ_i the potential B will evidently be equal to zero at equilibrium

$$U - TS + pV - \sum_i \mu_i N_i = 0, \quad (6.19)$$

since $U - TS + pV = Z$ and $\sum_i \mu_i N_i = Z$.

† A mechanical analogy of this case is the equilibrium of a sphere on a summit peak.

If T , p and μ_i are maintained constant while S , V and N_i are varied somewhat and have the values S' , V' and N'_i , then the state T , p , μ_i with coordinates S , V , N_i is stable if $\Delta B = B' - B > 0$ or, by taking (6.19) into account,

$$U' - TS' + pV' - \sum_i \mu_i N'_i > 0. \quad (6.20)$$

On the other hand an equilibrium state with coordinates S' , V' , N'_i (when the internal energy is equal to U') corresponds to determined values T' , p' , μ'_i ; therefore for such an equilibrium, similarly to (6.19) we have

$$U' - T'S' + p'V' - \sum_i \mu'_i N'_i = 0. \quad (6.21)$$

For a deviation of the system from this (assumed stable) state with given T' , p' and μ'_i , owing to S' , V' , N'_i becoming S , V , N_i we have, similarly to (6.20),

$$U - T'S + p'V - \sum_i \mu'_i N_i > 0. \quad (6.22)$$

Let us introduce the notation

$$\Delta T = T - T', \quad \Delta p = p - p', \quad \Delta \mu_i = \mu_i - \mu'_i. \quad (6.N)$$

By subtracting from (6.20) the equation (6.21) we shall obtain

$$-\Delta TS' + \Delta pV' - \sum_i \Delta \mu_i N'_i > 0, \quad (6.23)$$

and on subtracting from (6.22) the equality relation (6.19) we shall have

$$\Delta TS - \Delta pV + \sum_i \Delta \mu_i N_i > 0. \quad (6.24)$$

By adding up the inequalities (6.23) and (6.24) we finally obtain

$$\Delta T \Delta S - \Delta p \Delta V + \sum_i \Delta \mu_i \Delta N_i > 0, \quad (6.25)$$

where $\Delta S = S - S'$, $\Delta V = V - V'$ and $\Delta N_i = N_i - N'_i$. It can be seen from this that a state of a homogeneous system is stable, if for whatever fluctuation-type variation of whatever coordinate of the system, the thermodynamic forces corresponding to the other coordinates remaining constant, the following thermodynamic inequalities are satisfied

$$\left(\frac{\Delta T}{\Delta S} \right)_{p, \mu_i} = \frac{T}{C_{p, \mu_i}} > 0, \quad \left(\frac{\Delta p}{\Delta V} \right)_{T, \mu_i} < 0, \quad \left(\frac{\Delta \mu_i}{\Delta N_i} \right)_{T, p, \mu_j} > 0 \quad (k \neq i). \quad (6.26)$$

Thus the conditions for the stability of equilibrium of a physically homogeneous single-component system will be

$$C_p > 0, \quad \varepsilon_T = -V_0 \left(\frac{\partial p}{\partial V} \right)_T > 0, \quad (6.27)$$

i.e. the thermal capacity at constant pressure and the isothermal elasticity modulus at equilibrium must be positive.†

The condition $C_p > 0$ and therefore also $C_V > 0$ (see problem no. 96) has been obtained by us by having assumed the absolute temperature to be positive. On the other hand, however, as we have clarified in § 14, this condition expresses the definition of which temperature is larger and which smaller, and is the initial condition of such a definition. From this we conclude that the choice of a positive absolute temperature is connected with a definition (within the limits of quasi-static processes) of the concept "larger or smaller temperature".

Since, in addition, for $T > 0$ we arrive at the result of the flow of heat from a body of higher temperature to a body of lower temperature (§ 19), then we also see that the definition of larger or smaller temperature given in the analysis of quasi-static processes‡ and the definition of this concept given in the analysis of non-static processes†† are not independent from but are connected with each other: for $C_V > 0$ the absolute temperature for ordinary systems is always positive ($T > 0$). This connexion is established by the second law of thermodynamics by determining the stability condition of real bodies. In the light of these facts it is easy to understand the physical meaning of the stability conditions (6.27). In fact let for $T > 0$ the condition $C_p > 0$ be not satisfied and, on the contrary, C_p be negative. Then, in the presence of fluctuations leading to cession of heat by the system to the thermostat, the temperature of this system would increase, which would lead, in its turn, to a further cession of heat (since $T > 0$) and

† If the external parameter of the system is a and the generalized force associated with it is the quantity A , then, similarly to (6.27), the stability conditions of such a homogeneous system will be

$$C_A > 0, \quad \left(\frac{\partial A}{\partial a} \right)_T < 0. \quad (6.27')$$

‡ It is assumed that in communicating heat to a body under constant external parameters its temperature increases, i.e. $C_a > 0$.

†† If in the thermal contact of two bodies A and B , heat flows from A to B , then the temperature of the body A is higher than the temperature of the body B ; this definition is equivalent to $T > 0$.

therefore a system with $C_p < 0$ could not be in a stable state of equilibrium. Similarly, if instead of $(\partial p/\partial V)_T < 0$ we had $(\partial p/\partial V)_T > 0$, this would mean that for a small fluctuation-type decrease of volume the pressure in the system would decrease, this would cause a further volume contraction etc., and therefore the system would not be in equilibrium.†

The conditions (6.27) ensure the stability of equilibrium with respect to small fluctuations. In the presence of large fluctuations when specific features, not taken into account, of the surface of fluctuation-type initial stages begin to emerge, these conditions prove insufficient. For example the conditions (6.27) are satisfied in super-cooled vapour or super-heated liquid states, although these states are stable only for the formation, during density fluctuations, of small initial stages of a new phase, while in the presence of fluctuations with formation of large initial stages homogeneous systems are separated into two phases. This is caused by the special role of the surface energy of initial stages (which we have so far neglected); in the presence of small drops their formation leads to an increase of the free energy F of the system, and therefore these drops disappear, [whereas] in the presence of large initial stages their formation can lead to a decrease of F which leads to the separation of the system into two phases thus pointing to the metastability of a homogeneous system. This will be discussed in greater detail in the chapter on surface phenomena.

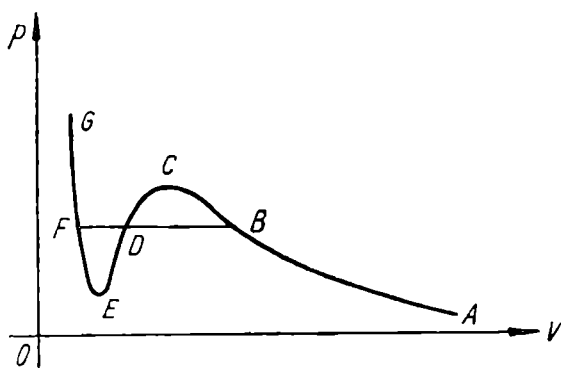


FIG. 24.

In connexion with the stability conditions obtained by us for a homogeneous system let us consider a system described by van der Waals' equation. Van der Waals' isotherm for temperatures below the critical temperature has the form shown in Fig. 24. The portion AB corresponds to gas, the portion FG to liquid. In these

states $(\partial p/\partial V)_T < 0$, which indicates their stability. States lying on the section CE are unstable since for them $(\partial p/\partial V)_T > 0$. The point C is the stability boundary of a gas phase, taken separately, with re-

† A case when $(\partial p/\partial V)_T = 0$ will be especially considered in § 41.

spect to its continuous variations (not connected with the formation of a new phase). Starting from the point B the gas begins, as a rule, to condense, and the state (a two-phase state) is determined by the rectilinear section BF . The sections BC and EF correspond to metastable states of supercooled vapour and superheated liquid respectively.

§ 32. Equilibrium in a homogeneous system

In a homogeneous system, as we have already observed, such processes are possible as: chemical reaction, dissociation, ionization, polymerization etc.

Let us consider the laws that govern the occurrence under equilibrium conditions of some of these processes.

1. *The condition of chemical equilibrium*

Every chemical reaction occurs generally speaking, both in the direct and reverse directions. Until equilibrium is reached the reaction in the direct direction prevails over the reverse one. At equilibrium the two opposite reactions proceed at the same rate so that the quantity of each kind of substance does not vary in the course of time. Let us find the equilibrium condition of a chemical system which is often called the condition of chemical equilibrium.

A chemical reaction is written in the form

$$\sum_i \nu_i A_i = 0, \quad (6.28)$$

where A_i are the chemical symbols of the reacting substances, and ν_i are the number of molecules of these substances (the stoichiometric coefficients). For example, for the reaction $2\text{SO}_2 + \text{O}_2 = 2\text{SO}_3$ or $2\text{SO}_2 + \text{O}_2 - 2\text{SO}_3 = 0$ the stoichiometric coefficients are $\nu_{\text{SO}_2} = 2$, $\nu_{\text{O}_2} = 1$, $\nu_{\text{SO}_3} = -2$.

Let a reaction proceed at constant temperature and pressure. In such a case, under equilibrium conditions, the thermodynamic potential Z of a system with a variable number of different particles has a minimum ($\delta Z = 0$), i.e.

$$-SdT + Vdp + \sum_i \mu_i dN_i = 0, \quad (6.0)$$

or

$$\sum_i \mu_i dN_i = 0, \quad (6.29)$$

since $T = \text{const}$ and $p = \text{const}$. The number of reacting molecules dN_i in the reaction are proportional to the numbers ν_i : $dN_1/dN_2 =$

$= \nu_1/\nu_2$, and therefore in (6.29) we can replace dN_i by ν_i . We shall then obtain the condition of chemical equilibrium

$$\sum_i \nu_i \mu_i = 0. \quad (6.30)$$

By comparing (6.28) and (6.30) we see that, in order to obtain the condition of chemical equilibrium we need to replace, in the equation of the chemical reaction, the symbols A_i by the corresponding chemical potentials μ_i . If several chemical reactions take place in the system, then equilibrium is determined by a set of equations of the form (6.30).

In order to apply the condition (6.30) to concrete chemical reactions we need to know expressions for the chemical potentials μ_i .

2. The law of mass action

The chemical potentials of gases are known except for the entropy constant. Therefore, by means of (6.25), we can establish a number of relations for chemical reactions in a mixture of ideal gases, when each gas behaves independently of the others and has a partial pressure p_i .

The chemical potential of an ideal gas is equal (see problem no. 88) to

$$\mu = kT \ln p + \mu_0(T). \quad (6.P)$$

In the case of a mixture of gases, we have for the i -th component $\mu_i = kT \ln p_i + \mu_{0i}(T)$ where p_i is the partial pressure of this component.

The total pressure of the mixture is $p = \sum p_i$. For an ideal gas $p_i = p N_i / \sum N_i = c_i p$, where c_i is the concentration of the i -th gas. Thus

$$\mu_i = kT \ln c_i p + \mu_{0i}(T), \quad (6.31)$$

and the condition of chemical equilibrium (6.30) for reactions in a gaseous mixture assumes the form

$$\sum_i \nu_i (kT \ln c_i p + \mu_{0i}(T)) = 0, \quad (6.Q)$$

whence

$$\left. \begin{aligned} kT \sum_i \nu_i \ln c_i + kT \sum_i \nu_i \ln p + \sum_i \nu_i \mu_{0i}(T) &= 0, \\ \sum_i \ln c_i^{\nu_i} &= - \sum_i \nu_i \ln p - \frac{1}{kT} \sum_i \nu_i \mu_{0i}(T) \end{aligned} \right\} \quad (6.R)$$

and

$$\prod_i c_i^{\nu_i} = p^{-\sum_i \nu_i} e^{-\frac{1}{kT} \sum_i \nu_i \mu_{0i}(T)} = K_c(T, p). \quad (6.32)$$

Assuming the ν_i 's to be positive for the substances entering in the reaction and negative for the substances obtained as a result of the reaction, (6.32) can be written in the form

$$\frac{\prod_j c_j^{\nu_j}}{\prod_s c_s^{\nu_s}} = K_c(T, p). \quad (6.33)$$

The equations (6.32) and (6.33) represent *the law of mass action*: The ratio of the product of the concentrations of the substances entering in a reaction to the product of the concentrations of the substances appearing as a result of reaction, the concentrations being raised to indices equal to the stoichiometric coefficients, is a constant quantity at constant temperature and pressure.

The quantity

$$K_c(p, T) = p^{-\sum_i \nu_i} e^{-(1/kT) \sum_i \nu_i \mu_{0i}(T)} \quad (6.34)$$

is called *the constant of chemical equilibrium*. The pressure dependence of $K_c(p, T)$ is fully determined by the factor $p^{-\sum \nu_i}$; to find the temperature dependence, however, requires further assumptions on the properties of gases (the temperature dependence of thermal capacities etc.). In the expression $\mu_{0i}(T)$ there occur entropy and energy constants. Both these constants have, of course, a fully determined value under equilibrium conditions. These values, however, cannot be determined on the basis of the two laws of thermodynamics, just as the value of the constant of chemical equilibrium $K_c(p, T)$ cannot. This problem is completely solved in statistical physics.

The law of mass action is valid also for reactions between dissolved substances, since weak solutions behave similarly to ideal gases.

If in a reaction the sum $\sum_i \nu_i$ is equal to zero, then $K_c(p, T)$ is altogether independent of pressure, as is the case, for example, in the dissociation of hydrogen iodide



The law of mass action can be expressed not only in terms of concentrations but also in terms of partial pressures, if in the equation of chemical equilibrium (6.30) we substitute $\mu_i = kT \ln p_i + \mu_{0i}(T)$. We shall then obtain

$$\prod_i p_i^{\nu_i} = K_p(T). \quad (6.35)$$

The equilibrium constant $K_p(T)$ is in this case altogether independent of pressure and depends only on temperature. In a number of cases this form of the law of mass action is the most convenient one.

3. Ostwald's law of dilution

In dissolving some substance (for example, common salt NaCl) in a solvent (in water) there occurs dissociation of this substance, i.e. the separation of molecules of the substance dissolved into positive and negative ions (Na^+ and Cl^-). At the same time together with this there also occurs a process of molization, i.e. the reunion of ions into neutral molecules. Under equilibrium conditions these two processes proceed at the same rate: as many molecules are dissociated as are molized. The dissociation phenomenon can be considered as a particular case of chemical reaction, and the equilibrium in the presence of dissociation can be considered as a particular case of chemical equilibrium.

Let us apply to this equilibrium the law of mass action. Dissociation is quantitatively characterized by the quantity $\alpha = n/N$, called *the degree of dissociation* (n is the number of dissociated molecules of the dissolved substance, and N is the total number of molecules of the dissolved substance).

Let the number of molecules of the solvent be equal to N_0 ; then the concentration of the solute is $c = N/N_0$, the concentration of positive ions of solute is $c_1 = n/N_0$, the concentration of negative ions of solute is $c_2 = n/N$, and the concentration of non-dissociated molecules of solute is $c_3 = (N - n)/N_0$.

By the law of mass action, under equilibrium conditions we have

$$\frac{c_1 \cdot c_2}{c_3} = K \quad (6.T)$$

(K is the dissociation constant), or

$$\frac{\frac{n}{N_0} \frac{n}{N_0}}{\frac{N-n}{N_0}} = \frac{\left(\frac{N}{N_0}\right)^2 \left(\frac{n}{N}\right)^2}{\frac{N}{N_0} \left(\frac{N-n}{N}\right)} = K, \quad (6.U)$$

whence

$$\frac{\alpha^2}{1-\alpha} c = K. \quad (6.36)$$

This equation represents *Ostwald's law of dilution*. It connects the dissociation coefficient α with the concentration of solute and shows that

as concentration decreases (i.e. as dilution increases) the degree of dissociation increases. In very weak solutions, when $c \rightarrow 0$, the degree of dissociation α tends to 1, i.e. nearly all molecules are dissociated.

The value of the dissociation coefficient α can be determined from the formula for the electric conductivity σ of a solution which is obtained in the theory of electrolytic dissociation

$$\sigma = F \alpha \eta (u_+ + u_-), \quad (6.V)$$

where F is Faraday's number, u_+ and u_- are the mobilities of positive and negative ions, and η is the equivalent concentration, equal to the number of gramme-equivalents of solute per unit volume of solvent.

The experimental confirmation of Ostwald's law of dilution is a good verification of the correctness of the theory of electrolytic dissociation.

§ 33. Equilibrium in a heterogeneous system

Let us now consider *the phase equilibrium* or *heterogeneous equilibrium* of a system consisting of n phases with k components. We shall qualify the quantities corresponding to different phases and components with two indices: the upper index will denote the phase and the lower index the component, so that, for example, μ_1'' denotes the chemical potential of the first component in the second phase.

1. *Equilibrium conditions of a heterogeneous system*

In § 30 we have established that, in a two-phase system of any substance whatsoever, equilibrium occurs for

$$T' = T'', \quad p' = p'', \quad \mu' = \mu'', \quad (6.37)$$

i.e. when temperatures, pressures and chemical potentials of the substance are the same in the two phases.

Similarly it can be shown (see problem no. 103) that in the equilibrium of two phases of different substances the following conditions must be satisfied

$$T'_1 = T''_2, \quad p'_1 = p''_2, \quad (6.38)$$

i.e. temperatures and pressures in the phases must be equal. In the equilibrium of phases of different substances the chemical potentials are subject to no conditions whatsoever, which is also physically evident without calculations since there can be no exchange of particles between such phases.

i.e. $2 + n(k - 1)$ variables. In order that the $k(n - 1)$ equations (6.41) may have solution it is necessary that their number be in each case not greater than the number of variables, i.e.

$$k(n - 1) \leq 2 + n(k - 1), \quad (6.X)$$

whence

$$n \leq k + 2. \quad (6.42)$$

This relation establishes the fact that in a system of k components not more than $k + 2$ phases can be found at the same time in equilibrium, and the relation itself is known as *Gibbs' phase rule*.

If the number n of phases in a thermodynamic system is smaller than $k + 2$, then in the equations (6.41) $k + 2 - n$ variables can evidently have arbitrary values. This means that $k + 2 - n$ variables can be varied without destroying equilibrium. The number of independent variables that can be arbitrarily varied without perturbing the equilibrium of a heterogeneous system is called *the number of thermodynamic degrees of freedom* f of the system; it is evident that

$$f = k + 2 - n. \quad (6.43)$$

Since the relation (6.43) is perfectly equivalent to (6.42), then also (6.43) is referred to as Gibbs' rule.

The phase rule in the form (6.42)

$$n \leq k + 2 \quad (6.Y)$$

has been obtained for a heterogeneous system on which there acts only the force of pressure p . If q generalized forces act on the system then, instead of the number 2 (corresponding to the variables p and T) the number $q + 1$ will figure in the rule of phases, and for such a system this rule will be written either in the form

$$n \leq k + q + 1, \quad (6.44)$$

or in the form

$$f = k + q + 1 - n. \quad (6.Z)$$

3. Curves of equilibrium of phases. The triple point

According to Gibbs' phase rule, in a system of k components not more than $k + 2$ phases can be found in equilibrium at the same time

$$n \leq k + 2. \quad (6.42)$$

In the case of a single-component system the maximum number of

phases that can be in equilibrium is equal to $n = k + 2 = 3$ and, in the case of a binary system, to $n = 4$.

In the equilibrium of two phases ($n = 2$) of a single-component substance ($k = 1$) the number of degrees of freedom is $f = k + 2 - n = 1$. This can also be seen from the equilibrium condition of the chemical potentials $\mu'(p, T) = \mu''(p, T)$, which connects the temperature and pressure in the phases.

One of these variables can be taken as the independent one and we shall then obtain the equation

$$p = p(T) \quad (6.45)$$

for the temperature dependence of pressure under equilibrium conditions. If we plot pressure and temperature along coordinate axes, then the points corresponding to phase equilibrium will lie on a certain curve (6.45) which is called *the curve of equilibrium of phases*. At the same time, points lying on different sides of this curve represent different homogeneous states of the body. For a variation of state along a line that intersects the curve of equilibrium (the dotted line in Fig. 25), phase differentiation occurs at the point of intersection

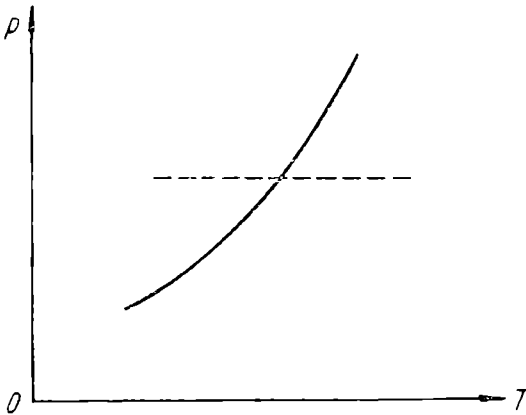


FIG. 25.

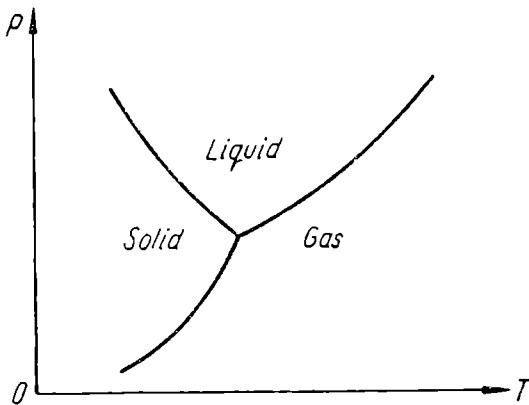


FIG. 26.

intersection and then the system passes to the other phase. The curve of equilibrium of phases is therefore the stability boundary of a phase with respect to its continuous variations.

For the equilibrium of three phases of one and the same substance we have two equations

$$\mu'(T, p) = \mu''(T, p), \quad \mu'(T, p) = \mu'''(T, p) \quad (6.AB)$$

with two variables. These equations give perfectly determined values of T and p for the equilibrium of three phases of one and the same sub-

stance. The state determined by these values of the variables T and p is called a *triple point*. On a T, p diagram the triple point is obtained as a result of the intersection of the curves of equilibrium of each three pairs of phases (Fig. 26). The triple point for water has the following values of T and p

$$t = 0.0078^\circ \text{C}, \quad p = 0.006 \text{ atm.} \quad (6. \text{AC})$$

Similar curves of the equilibrium of two phases can be obtained also for binary systems by representing, for example, the pressure of a two-phase binary system as a function of the concentration of one of the components in one of the phases.

4. *Equilibrium of binary systems. The fundamental equation of the theory of the equilibrium of binary systems*

Let us consider now the equilibrium between various phases with two independent components, i.e. the equilibrium of binary systems. Such systems have an important role in chemistry and metallurgy.

According to Gibbs' phase rule, the largest number of phases that can be found in equilibrium in the case of a binary system is equal to four. These four phases co-exist only at the quadruple point for which all parameters of the system (T , p and the phase compositions) are completely determined. In the case of co-existence of three phases the system has only one degree of freedom, i.e. one of the parameters can be chosen arbitrarily; such a parameter is usually pressure.

The most interesting case is the co-existence of two phases of a binary system, since other cases can be reduced to it. In a binary system two parameters can be chosen arbitrarily: we can assign, for example, temperature and the composition of one of the phases (the concentration of one of the components) and equilibrium will be possible for a determined pressure only; or else we can arbitrarily choose pressure and the composition of one of the phases; then there will be equilibrium only at a determined temperature. Let us establish the fundamental equation of the equilibrium of two phases of a binary system.

According to (5.64) we have for each phase

$$dU = T dS - p dV + \sum_i \mu_i dN_i. \quad (6. \text{AD})$$

Since, however,

$$Z = U - TS + pV \quad (6. \text{AE})$$

and

$$Z = \sum_i \mu_i N_i, \quad (5.72)$$

then

$$U = Z + TS - pV = \sum_i \mu_i N_i + TS - pV \quad (6.4F)$$

and

$$dU = \sum_i \mu_i dN_i + \sum_i N_i d\mu_i + T dS + S dT - p dV - V dp. \quad (6.46)$$

By comparing (5.64) and (6.46) we obtain the equation

$$S dT - V dp + \sum_i N_i d\mu_i = 0, \quad (6.47)$$

which is called the *Gibbs-Duhem equation*. Let us write this equation for two phases of a binary system:

$$\left. \begin{aligned} S' dT - V' dp + N'_1 d\mu_1 + N'_2 d\mu_2 &= 0, \\ S'' dT - V'' dp + N''_1 d\mu_1 + N''_2 d\mu_2 &= 0 \end{aligned} \right\} \quad (6.48)$$

(the phase indices are omitted for dT , dp and $d\mu$, since under equilibrium conditions $T' = T''$, $p' = p''$ and $\mu' = \mu''$).

Let us eliminate $d\mu_2$ from the equations (6.47). On multiplying the first equation by N'_2 and the second by N''_2 , we shall subtract the first equation from the second. We shall then obtain

$$(S''N'_2 - S'N''_2) dT - (V''N'_2 - V'N''_2) dp + (N'_1N''_2 - N'_2N''_1) d\mu_1 = 0. \quad (6.49)$$

This equation is the fundamental equation of the theory of a binary system; by using it we can establish all the laws of such systems. Of the greatest interest is the equilibrium of liquid binary solutions and their vapours.

The main laws of such binary systems have been established by D. P. Konovalov (see problem no. 106).

PROBLEMS

90. Deduce the equilibrium conditions of two phases from the condition for a minimum of the thermodynamic potential Z .

91. An ideal gas is found in an adiabatically isolated cylinder with a piston under the constant external pressure p_0 . By evaluating the entropy variations δS and $\delta^2 S$, show that under equilibrium conditions the entropy is actually a maximum.

92. Show that in a system with $S = \text{const}$ and $p = \text{const}$ equilibrium occurs for a minimum of enthalpy H , and for a system with $S = \text{const}$ and $V = \text{const}$ for a minimum of the internal energy U .

93. Show that the equilibrium of rays from various bodies in a cavity having specular walls is unstable, and establish that equilibrium radiation is a system of rays that are found in a stable equilibrium, with one and the same temperature for all rays.

94. Determine the equilibrium conditions of a system in an external field.

95. The conditions (6.27) for equilibrium stability were deduced for a small portion of a large homogeneous system. In which case are they valid and when are they invalid for the system as a whole?

96. Find concrete stability conditions of a homogeneous system in a thermostat at constant pressure, by proceeding from the general stability condition of such a system $\delta^2 Z > 0$.

97. If a state of an isotropic magnetic substance is characterized: (a) by the quantities H and B , then

$$dU = T dS - p dV + \frac{1}{4\pi} H dB, \quad (\text{A})$$

if, however, we use: (b) the quantities H and M , then

$$dU' = T dS - p dV + H dM, \quad (\text{B})$$

where

$$U' = U - \frac{H^2}{8\pi}. \quad (\text{6. AG})$$

According to the condition (6.27) for equilibrium stability: $(\partial A / \partial a)_T < 0$. For a magnetic substance this condition has the form: in the case (a) ($a = B$, $A = -H/4\pi$) $(\partial H / \partial B)_T = 1/\mu > 0$, which is in full agreement with experiment ($\mu > 0$); in the case (b) ($a = M$, $A = -H$) $(\partial H / \partial M)_T = 1/\kappa > 0$, which contradicts the experiment that shows the thermodynamic stability of diamagnetic substances although for them $\kappa < 0$. Explain the cause of this contradiction.

98. If a process in a system is caused by another process in the same system or by an external action, then the direction of such a process is determined by the *Le Chatelier-Braun principle*: every process that is caused in an equilibrium system by an external action or by another primary process is always so directed as to reduce the results of these actions. Establish this principle by using the equilibrium-stability conditions and adduce examples where this principle is shown.

99. Show that the temperature dependence of the equilibrium constant is determined by van't Hoff's equation

$$\left(\frac{\partial \ln K_c}{\partial T} \right)_p = - \frac{Q_p}{RT^2}, \quad (\text{6. AH})$$

where Q_p is the heat of reaction at constant pressure.

100. Show that the pressure dependence of the equilibrium constant is determined by the equation

$$\left(\frac{\partial \ln K_c}{\partial p} \right)_T = - \frac{\Delta V}{RT}, \quad (\text{6. AJ})$$

where ΔV is the volume increase of the mixture of reacting substances.

101. In the reaction for the formation of water-gas



equilibrium has set in at $T = 1259^\circ\text{K}$. The equilibrium molecular composition is known: $m_{\text{CO}_2} = 0.7$ mole, $m_{\text{CO}} = 9.46$ moles, $m_{\text{H}_2\text{O}} = 9.46$ moles, $m_{\text{H}_2} = 80.38$ moles. Determine the equilibrium constant K_p .

102. At a temperature $T = 717^\circ\text{K}$ the reaction of the formation of hydrogen iodide,



has reached equilibrium. By knowing the initial number of moles of iodine $m_{\text{I}_2} = 2.94$ moles and the initial number of moles of hydrogen $m_{\text{H}_2} = 8.1$ moles, determine the number of moles of HI at equilibrium. The equilibrium constant of the reaction for $T = 717^\circ\text{K}$ is known: $K_p = K_c = 0.01984$.

103. Determine the equilibrium condition of a two-phase system consisting of various substances.

104. By using the phase rule determine the number of thermodynamic degrees of freedom of a system consisting.

(a) of a water solution of KCl and NaCl in the presence of crystals of both salts and vapours;

(b) of a solution of these salts in the presence of ice, crystals of both salts and vapours.

105. Gibbs' phase rule has been established on the assumption that each component occurs in all phases. How is the phase rule modified if each component does not occur in all phases?

106. By considering, on the basis of the fundamental equation of the theory of the equilibrium of binary systems (6.49), a two-phase system of two volatile liquids and their vapours, establish *Konovalov's rules*: the vapour pressure of a mixture will increase with an increase of that component of which there is a higher concentration in the vapour phase (Konovalov's first rule); if a binary mixture is such that the vapour-elasticity curve of this system passes through a maximum or a minimum, then at these extrema the contents of liquid and vapour are the same (Konovalov's second rule).

CHAPTER VII

SURFACE PHENOMENA

IN ANALYSING the equilibrium of adjoining phases of a heterogeneous system we have so far neglected the special properties of the surface of separation and their influence on equilibrium. We have assumed that the internal energy U and the free energy F of a system that consists of two or several phases are equal to the sum of the internal energies or free energies of the individual phases. In this connexion each phase has been assumed to be homogeneous right up to the surface itself, and therefore the U and F of each phase have been assumed to be proportional to the mass of the phase.

However, in the surface layer of a phase of a thickness of the order of the radius of molecular interaction (10^{-7} cm), which is the boundary of the phase, where molecules interact not only with molecules of their own phase but also with the adjoining [surface] layer of another phase, the physical properties of the substance differ from the properties inside (in the volume of) the phase. Owing to this special property of the surface layer, the internal energy and free energy of a system are not additive functions.

Since the surface of a body increases in proportion to the square of the dimensions of this body, while its volume is proportional to the cube of these dimensions, then surface effects can be neglected for large bodies in comparison with volume effects and we can assume the energy of the system to be an additive function (i.e. proportional to the mass of the system), which is just what we have done so far. However, if a substance is found in a finely sub-divided state, then such a system has a widely extended surface, and therefore the neglecting of surface effects can lead in this case to substantial errors in the results of calculations. Surface effects are especially important for a correct approach to the problem of phase transitions (see Chap. VIII).

We shall set ourselves the task of taking into account the influence of a surface on the equilibrium of phases and on the formation of a new phase.

§ 34. Surface tension and surface pressure

The thermodynamics of surface phenomena was developed by Gibbs. He considered the surface layer as a new "surface phase" differing from the volume phases in that its thickness is extremely small in comparison with the extension in the other two dimensions and is equal in the limit to a single molecule. Such a model enables us to apply to a surface phase the general equations of heterogeneous equilibrium.

By considering phases of not very small dimensions, considerably larger than the radius of molecular interaction, we shall at first simplify the problem, by replacing the surface layer of finite thickness by an idealized infinitely thin surface of separation, dividing two phases from each other, and which we shall simply call surface. The value of the surface area, Σ , of a phase is a new parameter together with the volume V , characterizing the state of the system. An increase of the system surface at constant values of temperature and volume is accompanied by expenditure of work, since in order to form new surfaces some particles must pass from the volume to the surface, which is connected with work against the forces of molecular interaction.

We shall denote by σ the generalized force corresponding to the parameter Σ . Then the work (for $T = \text{const}$ and $V = \text{const}$) for an increase of surface by $d\Sigma$ is equal to

$$\delta W = -dF_{\Sigma} = -\sigma d\Sigma. \quad (7.A)$$

The quantity σ , which characterizes the equilibrium between two phases is called, as is known, the *surface tension* and is equal to the surface force per unit length on the surface or to the free energy of unit surface: $\sigma = dF_{\Sigma}/d\Sigma$. The surface energy is evidently equal to

$$U_{\Sigma} = F_{\Sigma} - T \frac{\partial F_{\Sigma}}{\partial T} = \sigma \Sigma - T \Sigma \left(\frac{\partial \sigma}{\partial T} \right)_{v, \Sigma} = \Sigma \left(\sigma - T \frac{\partial \sigma}{\partial T} \right). \quad (7.1)$$

Let us consider the equilibrium conditions in a system consisting of two phases divided by a surface of separation. We know that, when surface phenomena are neglected, the equilibrium conditions of two phases of one and the same substance are

$$T' = T'', \quad p' = p'', \quad \mu' = \mu''. \quad (7.2)$$

The same arguments as have been used to obtain (7.2), and which will not be repeated here, give for the equilibrium of two phases, when surface phenomena are taken into account, the equality relations

$$T' = T'', \quad \mu' = \mu''. \quad (7.B)$$

As to the pressures in the phases then, since the forces of surface tension are now taken into account at the boundary, equilibrium between the phases occurs for different pressures in the phases. Let us find this condition of mechanical equilibrium in a system of two phases: liquid ('), and vapour ("), by proceeding from the minimum of free energy for $T = \text{const}$ and $V = \text{const}$.

The differential of the free energy of a system consisting of liquid, vapour and surface of separation between them, when the temperature and the chemical potential in the phases are the same, is equal to

$$dF = -p' dV' - p'' dV'' + \sigma d\Sigma. \quad (7.3)$$

At equilibrium $dF = 0$, and therefore

$$\sigma d\Sigma - p' dV' - p'' dV'' = 0, \quad (7.C)$$

but since $V' + V'' = V = \text{const}$, then

$$p' = p'' + \sigma \frac{d\Sigma}{dV'}. \quad (7.4)$$

The quantity $d\Sigma/dV'$ determines the curvature of the surface of separation of the phases. In the case of a spherical surface we have

$$\frac{d\Sigma}{dV'} = \frac{d(4\pi r^2)}{d\left(\frac{4}{3}\pi r^3\right)} = \frac{2}{r} \quad (7.D)$$

(r is considered positive if the surface curvature is directed towards the (') phase). In the case of an arbitrary surface we have

$$\frac{d\Sigma}{dV'} = \frac{1}{r_1} + \frac{1}{r_2}, \quad (7.E)$$

where r_1 and r_2 are the principal radii of curvature of the surface. Thus, when spherical drops of liquid (') are in equilibrium with vapour (") the pressure in the drop, p' , and the vapour pressure, p'' , are connected by the condition

$$p' - p'' = \frac{2\sigma}{r} \quad (7.5)$$

and

$$p' = p'' + \frac{2\sigma}{r}. \quad (7.F)$$

From this it can be seen that on the surface of separation of two phases (drop-vapour) there exists a jump of pressure equal to $2\sigma/r$.

The quantity $\sigma(r_1^{-1} + r_2^{-1})$ or $2\sigma/r$ (in the case of a spherical surface is called *surface pressure* or *Laplace's pressure*. In the case of a plane surface ($r \rightarrow \infty$) separating liquid from vapour Laplace's pressure is equal to zero, and the condition of mechanical equilibrium now coincides with the corresponding condition not allowing for surface phenomena

$$p' = p'' . \quad (7.G)$$

§ 35. Equilibrium form of a crystal. Wulf's theorem

In the equilibrium of a crystal with its saturated vapour or with its melt, owing to the surface of separation the pressures in the crystal and in the surrounding medium are again not equal, and are connected by a relation similar to (7.5). This relation which was firstly obtained by the Russian crystallographer Iu. V. Vul'f (Wulf) in 1895, leads to Wulf's theorem on the mutual disposition of the faces of a crystal under equilibrium conditions. Similarly to (7.5) Wulf's theorem can be easily established by proceeding from the general equilibrium condition of a system for $T = \text{const}$ and $V = \text{const}$:

$$\delta F = 0, \quad \delta^2 F > 0. \quad (7.6)$$

Let us consider a monocrystal (the first phase) surrounded by its saturated vapour or melt (the second phase). By using (7.6) we shall find the condition of mechanical equilibrium between these two phases, the influence of the surface of separation being taken into account, by assuming the conditions already known of equality of the temperatures and chemical potentials of the phases. (These conditions also follow from (7.6), but we do not want to discuss their derivation here.)

The differential of the free energy of the system consisting of the crystal, the melt and the surface of separation between them, when the temperatures and chemical potentials in the phases are the same, is equal to

$$dF = -p_1 dV_1 - p_2 dV_2 + \sum_i \sigma_i d\Sigma_i, \quad (7.7)$$

where Σ_i is the surface of the i -th face of the crystal, and σ_i is its *specific surface energy*.† At equilibrium $dF = 0$, and therefore

$$\sum_i \sigma_i d\Sigma_i - p_1 dV_1 - p_2 dV_2 = 0 \quad (7.H)$$

† For the sake of brevity, we shall call the quantity σ_i , by analogy with a liquid, simply surface tension. One has to bear in mind, however, that this is not, generally speaking, quite the same, since the process of formation of a new crystal surface is connected in general with volume deformation.

and, since $V_1 + V_2 = V = \text{const}$,

$$\sum_i \sigma_i d\Sigma_i - (p_1 - p_2) dV_1 = 0. \quad (7.8)$$

We shall consider (Fig. 27) the volume of the crystal as the sum of volumes of pyramids built on the faces Σ_i , the apices of which converge to the centre of the crystal (h_i is the height of the i -th pyramid). It is evident that

$$V_1 = \frac{1}{3} \sum_i \Sigma_i h_i \quad (7.9)$$

and

$$dV_1 = \frac{1}{3} \sum_i (\Sigma_i dh_i + h_i d\Sigma_i). \quad (7.9)$$

On the other hand, every volume variation, except for a quantity of the second order of smallness, is equal to the surface Σ_i times the height variation dh_i

$$dV_1 = \sum_i \Sigma_i dh_i. \quad (7.10)$$

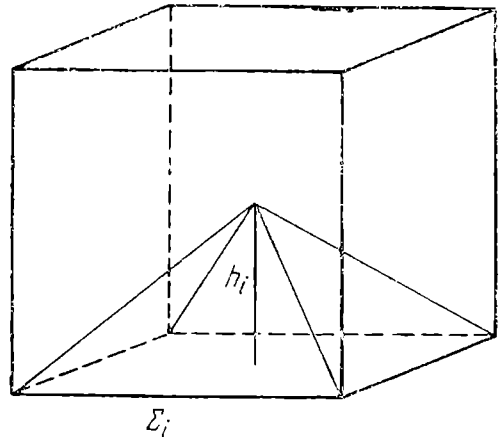


FIG. 27.

By comparing (7.9) and (7.10) we find

$$\sum_i \Sigma_i dh_i = \frac{1}{2} \sum_i h_i d\Sigma_i, \quad (7.K)$$

and therefore

$$dV_1 = \sum_i \Sigma_i dh_i = \frac{1}{2} \sum_i h_i d\Sigma_i. \quad (7.11)$$

By substituting (7.11) in (7.8) we shall have

$$\sum_i \left[\sigma_i - \frac{1}{2} (p_1 - p_2) h_i \right] d\Sigma_i = 0. \quad (7.12)$$

Since the variations $d\Sigma_i$ are independent, then from (7.12) we obtain the conditions of mechanical equilibrium

$$p_1 - p_2 = \frac{2\sigma_i}{h_i} \quad (i = 1, 2, \dots, n). \quad (7.13)$$

This condition is similar to (7.5) and therefore the quantity $2\sigma_i/h$ can be called, by analogy with Laplace's pressure, *Wulf's crystal surface pressure*.

On all crystal faces the differences $p_1 - p_2$ are the same, since otherwise the crystal would not be found at rest. We see from (7.13) that the equilibrium form of a crystal is determined by the equation

$$\frac{\sigma_1}{h_1} = \frac{\sigma_2}{h_2} = \dots = \frac{\sigma_n}{h_n} = \text{const} = W, \quad (7.13)$$

or

$$h_1 : h_2 : h_3 : \dots : h_n = \sigma_1 : \sigma_2 : \dots : \sigma_n, \quad (7.14)$$

which expresses *Wulff's theorem* on the mutual equilibrium disposition of the faces of a crystal: *under equilibrium conditions the faces of a crystal are removed from its centre by distances that are proportional to their specific surface free energies.*

If for a certain face $\sigma_i/h_i > W$, then it will evaporate or melt, whereas if $\sigma_i/h_i < W$ then such a face will grow, the crystal-growth rates u_i with respect to the normal to the various faces being proportional (in approaching equilibrium) to the specific surface free energies σ_i of these faces:

$$u_i = \frac{h_i}{t}, \quad h_i = \frac{\sigma_i}{W} \quad \text{and} \quad u_i \sim \sigma_i. \quad (7.15)$$

§ 36. The role of surface tension in the formation of a new phase. Initial stages

As is known, in the equilibrium of two phases of one and the same substance the chemical potentials of this substance are the same in the two phases

$$\mu_1(T, p_1) = \mu_2(T, p_2). \quad (7.16)$$

For a temperature or pressure variation the chemical potential (for example, of the liquid) will become larger than the chemical potential of the substance in the other phase (for example, the vapour), and this will now involve the passage of substance from one phase to the other (in the case given, evaporation). Thus, for example, water at atmospheric pressure boils as soon as its temperature reaches 100°C. At this point the chemical potential of water, increasing with a temperature increase, is found to be equal to the chemical potential of vapour.

It is well known, however, that by purifying a liquid such a condition can be reached that superheating of the liquid occurs, i.e. no phase transition takes place at temperatures considerably in excess of boiling temperature. A similar situation is observed also in the case of other phase transitions of the first kind:† in pure vapour

† These are such transformations of a substance from one phase to another that are connected with absorption or release of heat (melting, boiling etc.) (see Chapter VIII).

condensation is delayed (super-cooled vapour), in a pure liquid or solution the transition to crystalline state is delayed (oversaturation).

Within a certain range of temperatures and pressures a phase can exist the chemical potential of which has not a minimum value. Such a state of a system is metastable. After some time has elapsed the system must pass to a stable state with a minimum value of the chemical potential. This transition, however, is made difficult for the reason that in the presence of small drops the surface free energy F_Σ , proportional to R^2 , increases more rapidly than the volume term of the potential, proportional to R^3 , decreases. Therefore the growth of small drops is not favoured thermodynamically, since it leads to an increase of thermodynamic potential, a fact which makes condensation impossible. In the presence of large drops, however, starting from a certain $R = R_c$ the volume term decreases, on the contrary, more rapidly than the surface term increases, and thus condensation becomes possible: having once arisen as a result of fluctuations such a drop will increase.

For each metastable phase certain minimum dimensions exist that an accumulation of another phase arising within the former as a consequence of fluctuations must possess, in order that this other phase may prove to be a stable initial phase. For smaller dimensions the fundamental phase remains more stable than these fluctuations and these disappear. Such accumulations of a new phase possessing minimum dimensions are called *initial stages*.

Let us evaluate the critical radius of a drop for vapour to condense. We shall assume that, as a result of fluctuation occurring in the old phase the centre of a new phase has been formed, for example a little drop of radius R in vapour. Since in the general case $Z = F + Aa$ and $\Delta F = \Delta Z - \Delta(Aa)$ then, in the case considered ($A = -\sigma, a = \Sigma$), the variation of free energy of the system for the formation of a drop will be equal to

$$\Delta F = (\mu_2 - \mu_1) N + \sigma \Sigma, \quad (7.15)$$

where μ_1 is the chemical potential of the old phase (vapour), μ_2 is the chemical potential of the new phase (drop), N is the number of particles in the new phase, Σ is the surface of the new phase, and σ is the surface tension.

The quantities N and Σ can easily be expressed in terms of the radius of the drop

$$\Sigma = 4\pi R^2, \quad N = \frac{4\pi R^3}{3v_2}, \quad (7.0)$$

where v_2 is the volume corresponding to one particle in the new phase. Thus we have

$$\Delta F = 4\pi (\mu_2 - \mu_1) \frac{R^3}{v_2} + 4\pi \quad (7.16)$$

It follows from this formula that two cases are possible:

(1) $\mu_2 > \mu_1$, (2) $\mu_2 < \mu_1$.

In the first case the new phase has a chemical potential larger than the old one and is the less stable. The occurrence of a little drop of liquid in vapour (or of a bubble in liquid) leads, whatever its R dimension, to an increase of ΔF (Fig. 28), and therefore the formation of a new phase is thermodynamically handicapped. If, as a result of fluctuations, a drop in such a vapour does arise then, whatever dimensions it might have, it must rapidly vanish. In the second case ($\mu_2 < \mu_1$) the second phase (of large dimensions) is the more stable thermodynamically. Also in this case, however, as the dimensions of the arising fluctua-

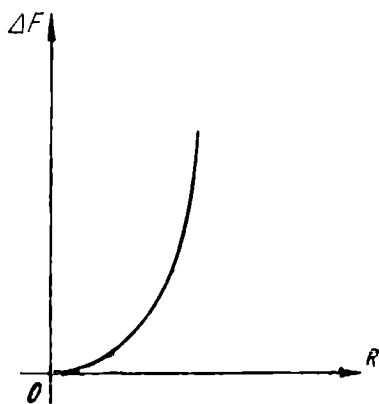


FIG. 28.

tion of the second phase increase, the value of ΔF at first (as long as $R < R_c$) increases, so that small fluctuations of the new phase are unstable (Fig. 29). This instability, as we have already said above, is explained by the fact that for small values of R the second term in the expression for ΔF increases with an increase of R more than the first term decreases.

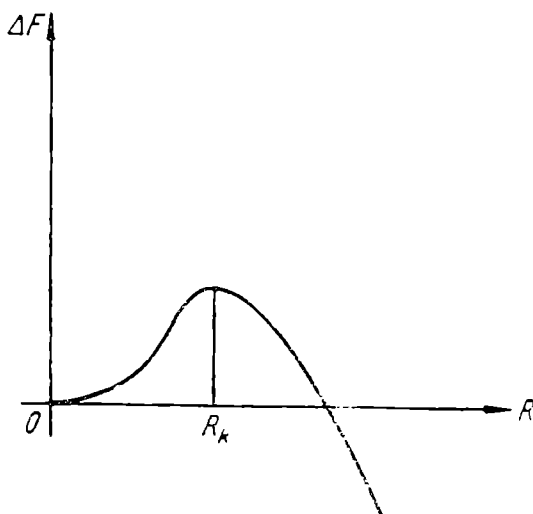


FIG. 29.

We shall find the dimensions of an initial stage by proceeding from the condition of a maximum of the variation of free energy ΔF (which expresses the condition of unstable equilibrium)

$$\left. \frac{\partial (\Delta F)}{\partial R} \right|_{R=R_c} = 0 \quad (7.17)$$

or

$$4\pi \frac{\mu_2 - \mu_1}{v_2} R_c^2 + 8\pi\sigma R_c = 0, \quad (7.Q)$$

whence

$$R_c = \frac{2\sigma v_2}{\mu_1 - \mu_2}. \quad (7.17)$$

It can be seen from this that the critical radius of an initial stage is proportional to the coefficient of surface tension. The term $\mu_1 - \mu_2$ in the denominator shows that the larger the supersaturation of vapour (the larger this difference) the smaller will be the critical radius and the sooner will condensation begin.

A similar situation also occurs in the case of other phase transitions of the first kind; in the boiling of liquid these initial stages are bubbles of vapour, and in crystallization—crystallites. In these cases, however, not only bubbles or crystallites of the given substance but also particles of an extraneous substance (contaminations) can have the role of initial stages.

§ 37. Gibbs' equation for adsorption.

Surface-active substances

In the equilibrium of a heterogeneous system, on the surface of separation of various phases there is observed a variation of the concentrations of the components of the system. Gases tend to thicken on solid surfaces, and dissolved substances also accumulate on similar surfaces. This phenomenon is the consequence of the tendency of the free surface energy to become as small as possible; the concentration in a surface layer varies in such a manner as to reduce the free surface energy.

A variation of concentration on a surface of separation is called *adsorption*; it is *positive* if the concentration of the solute is larger on the surface than in the solution, and is *negative* if the concentration on the surface is smaller.

Let us find the connexion between the value of adsorption and surface tension.

Following Gibbs, we shall consider a surface layer as a new phase. Let N_i be the excess of concentration of the i -th component in this phase. Then the variation of free energy of the phase for an indefinitely small increase of the surface Σ and of the numbers N_i (at constant temperature and volume) is equal to

$$dF = \sigma d\Sigma + \sum_i \mu_i dN_i. \quad (7.18)$$

Hence

$$d(F - \sum_i \mu_i N_i) = \sigma d\Sigma + \sum_i N_i d\mu_i \quad (7.19)$$

and, since the left-hand side of the equation is a total differential

$$\left(\frac{\partial \sigma}{\partial \mu_i} \right)_\Sigma = - \left(\frac{\partial N_i}{\partial \Sigma} \right)_{\mu_i}. \quad (7.20)$$

The quantity

$$\Gamma_i = \left(\frac{\partial N_i}{\partial \Sigma} \right)_{T, v, \mu} = \frac{N_i}{\Sigma} \quad (7.21)$$

represents the excess of concentration of the i -th component per unit surface (the value of the adsorption of the i -th component). Thus

$$\Gamma_i = - \left(\frac{\partial \sigma}{\partial \mu_i} \right)_\Sigma. \quad (7.22)$$

This relation expresses the value of the adsorption of a substance in terms of the derivatives of the surface tension with respect to its chemical potential and is called *Gibbs' equation for adsorption*.

In the case of an ideal solution, when the chemical potential, according to (6.31), is equal to

$$\mu_i = \mu_0 + kT \ln c_i \quad \text{and} \quad d\mu_i = kT \frac{dc_i}{c_i}, \quad (7.R)$$

Gibbs' equation assumes the form†

$$\Gamma_i = - \frac{c_i}{kT} \left(\frac{\partial \sigma}{\partial c_i} \right) \quad (7.23)$$

or

$$\Gamma_i = - \frac{c_i}{RT} \left(\frac{\partial \sigma}{\partial c_i} \right). \quad (7.24)$$

It can be seen from these equations that in a surface layer there will accumulate chiefly those substances the presence of which lowers the surface tension ($\Gamma_i > 0$ for $\partial\sigma/\partial c_i < 0$). Such substances by their presence lower the free energy of the surface layer and, since this is thermodynamically favourable for equilibrium, then this also explains their positive adsorption (surface-active substances). Those substances, however, whose presence causes an increase of surface tension ($\partial\sigma/\partial c_i > 0$) tend to leave the surface layer ($\Gamma_i < 0$, negative adsorption), since by their presence they increase the surface free energy.

† In (7.24) the value of the adsorption Γ_i is not expressed by the number of particles of the i -th component per unit surface, as in (7.23), but by the number of moles of this component.

It is found that small additions of certain surface-active substances are sufficient to modify markedly the properties of a body. This fact is widely used in practice in metallurgy and electronics. By means of small additions of surface-active substances the strength of metals is increased. In addition, since the work function of electrons in a metal is determined by the surface tension, then the addition of a small quantity of surface-active substances can markedly reduce the work function of electrons, which fact is of great importance in the photo-effect.

Surface-active substances have recently found wide application in the extraction of oil. The decrease of the quantity of oil given by an oil well per unit time when the well is filled with water is due to the fact that drops of water are retained in the narrowings of the porous channels of the rock of the oil field. The resistance of these drops is proportional to their surface tension and can reach large values. This resistance must be overcome by the parallel flow of the surrounding oil phase. The pressure in the layer, however, is far from sufficient for this. The lowering by means of surface-active substances of the surface tension on the water-oil boundary, enables the extraction of oil to be made considerably cheaper. Surface-active substances are also used in the washing out of sandstone blocking in oil wells.

PROBLEMS

107. Determine how the saturated vapour pressure on a drop depends on the drop's radius.

108. Show that a very small charged drop will increase not only in super-saturated vapour, but even in vapour that has not reached saturation (which is used in the Wilson chamber for detecting traces of fast ionizing particles).

109. Similarly to Gibbs' equation for adsorption (7.22), find the connexion between the electric charge on a unit surface of solution of an electrolyte and its surface tension.

CHAPTER VIII

PHASE TRANSFORMATIONS AND CRITICAL PHENOMENA

FOR A VARIATION of state of an equilibrium heterogeneous system, a substance can pass from one phase to another phase, for example from liquid to vapour, from one crystal form to another, from normal-conductor to super-conductor state, from ferromagnetic to paramagnetic state etc. Such transitions of a substance from one phase to another for a variation of state of a system are called *phase transformations*.

Of the greatest practical and theoretical interest are phase transformations in single-component and binary systems. We shall consider phase transformations only in single-component heterogeneous systems.

Under equilibrium conditions, and therefore also in phase transformations, the chemical potentials of a substance in the phases and the temperatures of the phases are always equal. As to certain other thermic and caloric quantities (or the derivatives of various orders of the thermodynamic (or chemical) potential with respect to them) they in general undergo jumps in phase transformations.

According to Ehrenfest the order of a phase transition is determined by the order of the derivatives of the thermodynamic potential that undergo *finite* variations at the transition point. Phase transformations for which the first derivatives of the thermodynamic potential Z (i.e. the volume $V = (\partial Z / \partial p)_T$ and the entropy $S = -(\partial Z / \partial T)_p$) undergo jumps are called *phase transitions of the first kind*; phase transitions for which the first derivatives of Z are continuous but its second derivatives (the thermal capacity $C_p = -T(\partial^2 Z / \partial T^2)_p$, the compressibility $\beta = -V_0^{-1}(\partial^2 Z / \partial p^2)_T$, the coefficient of thermal expansion $\alpha = V_0^{-1}(\partial^2 Z / \partial T \partial p)$) undergo jumps are called *phase transitions of the second kind* etc.

It can be seen from these definitions that in phase transitions of the first kind there occurs absorption (or release) of latent heat $Q = T(S'' - S')$, whereas phase transitions of the second kind are not accompanied by heat or volume effects.

We are aware today of phase transitions of the first kind (melting, evaporation, transitions from one crystal form to another etc.), and also phase transitions of the second kind (the transition of a conductor from normal to super-conducting state, the transition of iron at Curie's point from ferromagnetism to paramagnetism etc.). As to transitions of higher orders, for example phase transitions of the third kind, thermodynamics and statistical physics show them to be possible in principle but mark them as extremely rare. So far these transitions have not been observed experimentally.

A common distinctive feature of phase transitions of various types consists in that, in approaching the transition point there occur considerable anomalies in the temperature behaviour of a series of characteristics of the substance (thermal capacity, coefficient of thermal expansion, heat contents etc.). The nature, however, of these anomalies is completely different for phase transitions of the various types. Thermodynamics cannot indicate the form and nature of these anomalies. The problem of the nature of the anomalous phenomena in the vicinity of the melting point is today at the solution stage.

The experimental investigation of phase transitions is a rather complicated task. Difficulties are encountered particularly often in assessing measurements of enthalpy and entropy connected with melting extended over a temperature interval ("premelting"). A first attempt at a theoretical clarification of the nature of premelting and the anomalies in melting (the thermal capacity C_p and the coefficient of expansion in a number of bodies increase by 10 to 20 and more times in an interval of 3 to 5°C in the vicinity of the melting point) has been based on taking the influence of impurities into account. A number of experiments, however, contradict this approach; thus in the artificial "contamination" of paraffin (in the melted state) by various impurities, no deviations whatsoever of the thermal capacity and other properties from their values in a pure crystal are observed.

Ia. I. Frenkel (1939) refuted the "impurity theory" and explained premelting on the basis of his theory of heterophasic fluctuations.† According to this theory, in the vicinity of melting temperature in a crystal there is a stable number of initial stages of the liquid phase, the system becomes dispersive with an extended surface, and this

† If fluctuations lead to the transition of a given molecular complex to another phase, they are called heterophasic, to distinguish them from fluctuations in which a molecular complex, in spite of variation of its energy, remains within the limits of the previous phase (and which, therefore, are called homophasic fluctuations).

basically determines the peculiarities of the behaviour of the system. It has been shown theoretically that quantitatively the effects caused by impurities do not correspond at all to the anomalies observed. However, an experimental investigation of the melting process in pure mercury and in mercury with impurities (zinc, thallium) has established† the absence of anomalies of thermal capacity in the melting of pure mercury and the presence of considerable anomalies of C_p in mercury with impurities. The contradiction arising (impurities cannot by themselves explain anomalies, but at the same time there are no anomalies without impurities) can be removed by assuming that impurities only serve as a "priming" for the development of a fluctuation process, as centres of formation of initial stages; in a similar manner to impurities, electrical discharges and other inhomogeneities serve as centres of crystallization in a supercooled liquid.‡ In the melting of bodies with little heat conversion, impurities have an essential "priming" role for premelting and anomalies.

In a thermodynamic analysis of phase transitions the role of fluctuations and surface effects, which lead to a series of important distinctive features of phase transitions, can only be indicated qualitatively.

§ 38. Phase transitions of the first kind.

Clapeyron–Clausius equation

1. The fundamental equation that characterizes phase transitions of the first kind is the Clapeyron–Clausius equation. This equation is obtained from the condition that the chemical potentials in the equilibrium of two phases are equal:

$$\mu'(T, p) = \mu''(T, p) \quad (8.1)$$

it connects with each other the heat of transition, the jump of specific volume and the slope of the equilibrium curve at the transition point.

The equation of the equilibrium curve follows from (8.1)

$$p = p(T). \quad (8.2)$$

Since we do not know the concrete form of the function $\mu(T, p)$ we are not in a position, either, to write down the equation of the equilibrium curve (8.2) in explicit form. It is found, however that the diffe-

† V. N. Kostryukov and P. G. Strelkov; Melting, premelting and false phase transition, *Zh. fiz. khimii* 28, No. 10, 1825 (1944).

‡ V. Yu. Urbakh; On the role of impurities in premelting phenomena, *Zh. fiz. khimii* 31, No. 9, 2147 (1957).

rential equation of the equilibrium curve has a much simpler form and connects with each other the above-mentioned quantities, which can be easily measured. By differentiating (8.1) we have

$$d\mu'(T, p) = d\mu''(T, p) \quad (8.A)$$

or

$$\left(\frac{\partial\mu'}{\partial T}\right)_p dT + \left(\frac{\partial\mu'}{\partial p}\right)_T dp = \left(\frac{\partial\mu''}{\partial T}\right)_p dT + \left(\frac{\partial\mu''}{\partial p}\right)_T dp, \quad (8.B)$$

whence

$$\frac{dp}{dT} = \frac{\left(\frac{\partial\mu''}{\partial T}\right)_p - \left(\frac{\partial\mu'}{\partial T}\right)_p}{\left(\frac{\partial\mu'}{\partial p}\right)_T - \left(\frac{\partial\mu''}{\partial p}\right)_T} \quad (8.C)$$

and

$$\frac{dp}{dT} = \frac{s'' - s'}{v'' - v'}, \quad (8.3)$$

since $d\mu = -sdT + vdp$ (s and v are the entropy and volume for a single particle). The equation (8.3) is the differential equation of the equilibrium curve and is called the *Clapeyron–Clausius equation*. More often it is written in the form

$$\frac{dp}{dT} = \frac{\lambda}{T(v'' - v')}, \quad (8.4)$$

where $\lambda = T(S'' - S')$ is the heat of transition per mole or per gramme of substance, and $v'' - v'$ is the volume variation of this quantity of substance.

If the system is acted on not by the force of pressure p but by some other generalized force A , we obtain the *general equation of the equilibrium of two phases* of a single-component system

$$\frac{dA}{dT} = \frac{\Delta S}{\Delta a}, \quad (8.5)$$

where $\Delta S = S'' - S'$ is the variation (the jump) of entropy for the passage of the substance from one phase to another, and $\Delta a = a'' - a'$ is the jump of the external parameter associated with the generalized force A .

2. The Clapeyron–Clausius equation

$$\frac{dT}{dp} = \frac{T(v'' - v')}{\lambda} \quad (8.D)$$

determines the temperature variation of a phase transition (for example the variation of the freezing or the boiling point) for a variation of pressure.

Since in the transition of liquid to vapour heat is communicated to the system ($\lambda > 0$) and the volume always increases ($v'' > v'$), it follows that $dT/dp > 0$, i.e. the boiling temperature always increases for an increase of pressure. The melting point, however, ($\lambda > 0$) can either increase or decrease for an increase of pressure, depending on whether volume increases or decreases in melting. In the majority of bodies $v'' > v'$ at melting and, therefore in such bodies, just as in the case of boiling, $dT/dp > 0$. However, in water, cast iron and bismuth the volume decreases with the melting of the solid phase, so that $dT/dp < 0$ for them, i.e. the melting point decreases with an increase of pressure.

In secondary-school physics an efficacious experiment is demonstrated by means of ice and a wire with a weight, which confirms this behaviour of the melting point in ice. In nearly all textbooks this property of ice is used for explaining in the following manner the slipperiness of ice, i.e. the known fact that skating on ice is easy in winter: as a consequence of the large pressure exerted by the blades of skates the ice melts at a temperature below 0°C ; this provides a watery lubricant which is responsible for the slipperiness of ice.

Such an explanation of the slipperiness of ice was given about 100 years ago by the English physicists Tyndall and Reynolds, and has been widely accepted although it does not at all correspond to the facts.

It follows, in fact, from the Clapeyron–Clausius equation that in order to lower the melting point of ice by only a few degrees, such a high pressure is needed that the ice would not be capable of sustaining it. In fact the specific volume of ice at 0°C is $v' = 1.091 \text{ cm}^3/\text{g}$, and that of water is $v'' = 1 \text{ cm}^3/\text{g}$. The heat of melting is $\lambda = 80 \text{ cal/g}$. Therefore

$$\frac{dp}{dT} = -\frac{\lambda}{T(v'' - v')} = -\frac{80 \times 41.3}{273 \times 0.091} \text{ atm}/^\circ\text{C} = -134 \text{ atm}/^\circ\text{C} \quad \left. \vphantom{\frac{dp}{dT}} \right\} \text{ (S.E.)}$$

(1 cal = $41.3 \text{ atm} \cdot \text{cm}^3$),

i.e. for lowering the melting temperature of ice by 1°C , the pressure must be increased by 134 atmospheres. And for ice to begin to melt, for example at -10°C the pressure must be increased on the average to 1300 atm; the ice cannot sustain such a pressure!

As has now been conclusively shown by experiment,[†] the slipperiness of ice is caused by the formation in the sliding plane of a watery lubricant due to the conversion into heat of the work of the motive forces overcoming friction.

3. Thermodynamics considers phase transitions as point phenomena (at a temperature T_0 and pressure p_0). In reality, however, as a consequence of heterophasic fluctuations the temperature point of a phase transition is blurred into a certain small interval.

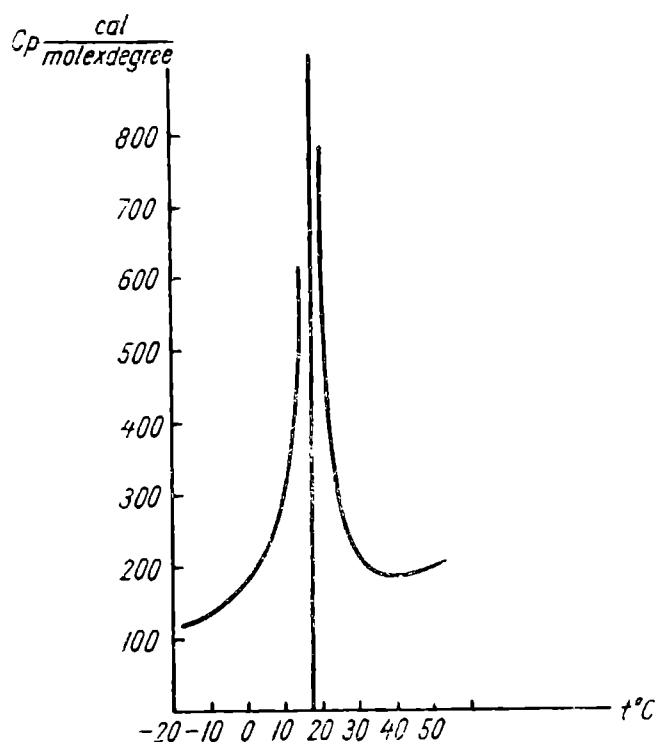


FIG. 30.

In the thermodynamic approach to a phase transition of the first kind we establish that the thermal capacity at the transition point is equal to infinity:

$$C_p = \left(\frac{\delta Q}{dT} \right)_p, \quad \text{but } \delta Q \neq 0, \quad \text{and } dT = 0, \quad (8.F)$$

and therefore

$$C_p = \infty. \quad (8.6)$$

It has been observed experimentally that in approaching the melting point (both on the side of the solid phase $T' < T_0$ and on the side of

[†] S. S. Budnevich and B. V. Deryagin; *Zh. tekhn. fiz.* 22, page 1967 (1962).

the liquid phase $T'' > T_0$) the curves that represent the temperature behaviour of the thermal capacity bend rapidly upwards (see Fig. 30 on which is shown the temperature dependence of the thermal capacity of paraffin in the neighbourhood of the melting point). Such a behaviour of the thermal capacity in phase transitions of the first kind agrees with that which the theory of heterophasic fluctuations predicts.

In phase transitions of the first kind a system, being dispersive, has a highly developed surface. The taking into account of the surface leads, as we have seen in Chapter VII to the fact that the system can be found in the vapour state at pressures exceeding the saturation pressure at the given temperature. This possibility of the existence of supercooled or superheated phases (supercooled vapour, superheated liquid) is the typical distinctive feature of phase transitions of the first kind.

§ 39. Phase transitions of the second kind.

Ehrenfest's equation

In phase transitions of the second kind no heat is absorbed and the specific volume does not vary ($s' = s''$, $v' = v''$) but the thermal capacity c_p , the coefficient of thermal expansion α and the compressibility β undergo jumps. The connexion between these jumps and the slope of the equilibrium curve at the transition point is determined by Ehrenfest's equations, who first introduced (1933) the concept itself of phase transitions of the second kind in an analysis of the He-I to He-II transition.† Let us derive these equations. The right-hand side of Clapeyron-Clausius equation

$$\frac{dp}{dT} = \frac{s'' - s'}{v'' - v'} \quad (8.3)$$

at the point of a phase transition of the second kind assumes the indeterminate form 0/0. In order to resolve this indeterminacy we shall use L'Hôpital's rule. By differentiating the numerator and denominator

† The form of the curve of the temperature variation of the thermal capacity in the vicinity of the He-I to He-II transition point recalls the specular image of the Greek letter λ (lambda) and therefore this curve is called a λ -curve, and the transition point the λ -point. The presence of a λ -point on the curve of the thermal capacity has come to be considered as the distinguishing feature of a phase transition of the second kind.

of the right-hand side of (8.3) with respect to either T or p we shall obtain

$$\frac{dp}{dT} = \frac{\frac{\partial s''}{\partial T} - \frac{\partial s'}{dT}}{\frac{\partial v''}{dT} - \frac{\partial v'}{\partial T}} = \frac{\Delta c_p}{T \Delta \left(\frac{\partial v}{\partial T} \right)_p} \quad (8.7)$$

and

$$\frac{dp}{dT} = \frac{\frac{\partial s''}{\partial p} - \frac{\partial s'}{\partial p}}{\frac{\partial v''}{\partial p} - \frac{\partial v'}{\partial p}} \quad (8.6)$$

or

$$\frac{dp}{dT} = - \frac{\Delta \left(\frac{\partial v}{\partial T} \right)_p}{\Delta \left(\frac{\partial v}{\partial p} \right)_T}, \quad (8.8)$$

since from $d\mu = -sdT + vd p$ it follows that $-(\partial s/\partial p)_T = (\partial v/\partial T)_p$. From (8.7) and (8.8) we obtain Ehrenfest's equations

$$\Delta c_p = -T \left(\frac{dp}{dT} \right)^2 \Delta \left(\frac{\partial v}{\partial p} \right)_T, \quad (8.9)$$

$$\Delta \left(\frac{\partial v}{\partial T} \right)_p = - \frac{dp}{dT} \Delta \left(\frac{\partial v}{\partial p} \right)_T. \quad (8.10)$$

If not only the force of pressure p but also some other generalized force A corresponding to the external parameter a acts on the system, then Ehrenfest's equation will have the form

$$\Delta c_A = -T \left(\frac{dA}{dT} \right)^2 \Delta \left(\frac{\partial a}{\partial A} \right)_T, \quad (8.11)$$

$$\Delta \left(\frac{\partial a}{\partial T} \right)_A = - \frac{dA}{dT} \Delta \left(\frac{\partial a}{\partial A} \right)_T. \quad (8.12)$$

Let us apply these equations to the case of the transition of a conductor from normal (n) to superconducting (s) state. As is known, such transitions occur in some conductors at a determined temperature T_c . Superconductivity can be destroyed if a sufficiently intense magnetic field H_c is superimposed. The temperature dependence of the critical field H_c is analogous to the temperature dependence of pressure $p =$

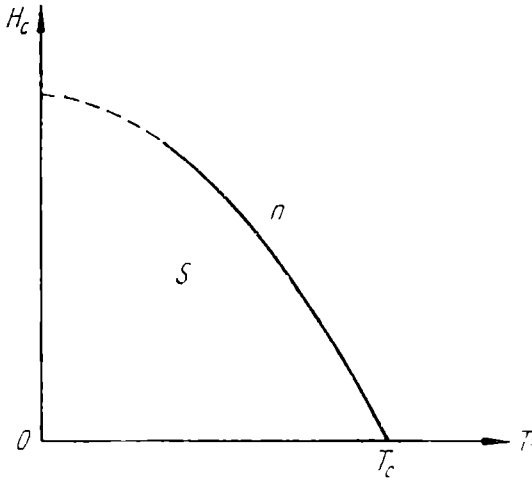


FIG. 31.

$= p(T)$ in liquid-vapour equilibrium and is represented on the H, T diagram by the curve shown in Fig. 31 (a sufficiently accurate analytical representation of this curve is the parabola $H_c(T) = H_c[1 - (T/T_c)^2]$). If a conductor is placed in a magnetic field its transition to superconducting state is accompanied by a heat effect, and therefore it is a phase transition of the first kind. It has

been shown by Keesom that the transition is determined in this case by the Clapeyron-Clausius equation. In the absence of a magnetic field the heat of transition is equal to zero and the n -to- s transition is a phase transition of the second kind†.

By putting in the equation (8.11) $A = H$ and $a = -M$ we shall obtain for the jump of the thermal capacity‡

$$\Delta c = c_s - c_n = -T \left(\frac{dH}{dT} \right)_{H=0}^2 \Delta \left(\frac{\partial M}{\partial H} \right)_T. \quad (8.13)$$

For a normal conductor $M_n = (\mu - 1)H/4\pi$, and for a superconductor $\mu = 0$ and $M_s = -H/4\pi$. Thus

$$\left(\frac{\partial M_s}{\partial H} \right) = -\frac{1}{4\pi}, \quad \frac{\partial M_n}{\partial H} = \frac{\mu - 1}{4\pi} \quad (8.H)$$

and

$$\Delta \left(\frac{\partial M}{\partial H} \right) = \frac{\partial M_s}{\partial H} - \frac{\partial M_n}{\partial H} = -\frac{\mu}{4\pi}. \quad (8.J)$$

However, $\mu = 1 + 4\pi\kappa$, and κ for paramagnetic and diamagnetic substances is of the order of 10^{-5} to 10^{-6} , and therefore

$$\Delta \left(\frac{\partial M}{\partial H} \right) = -\frac{1}{4\pi} \quad (8.K)$$

† The modern microscopic theory of superconductivity due to Bardeen-Cooper-Schrieffer and Bogolyubov leads to a finite jump of thermal capacity in the transition of superconducting metals from normal to superconducting state.

‡ The minus sign in (8.13) is retained in such a substitution since in (8.8), from which (8.11) is obtained, there must be a plus sign if the variables are H and M .

and

$$c_s - c_n = \frac{T}{4\pi} \left(\frac{dH}{dT} \right)_{H=0}^2. \quad (8.14)$$

This formula is called *Rutgers's formula*. It agrees to a high degree of accuracy with experimental data, as can be seen from the following table.

Substance	Experimental value <i>cal</i> degree \times mole	Calculated value <i>cal</i> degree \times mole
Tin	0.00290	0.00261
Thallium . . .	0.00148	0.00146
Indium	0.00202	0.00201

The temperature behaviour of the thermal capacity of tin in its transition to superconducting state (in the absence of a magnetic field) is represented by the curve shown in Fig. 32 according to Keesom's data. This curve has little in common with the λ -curve. Thus in this phase transition of the second kind there is no overshooting of the

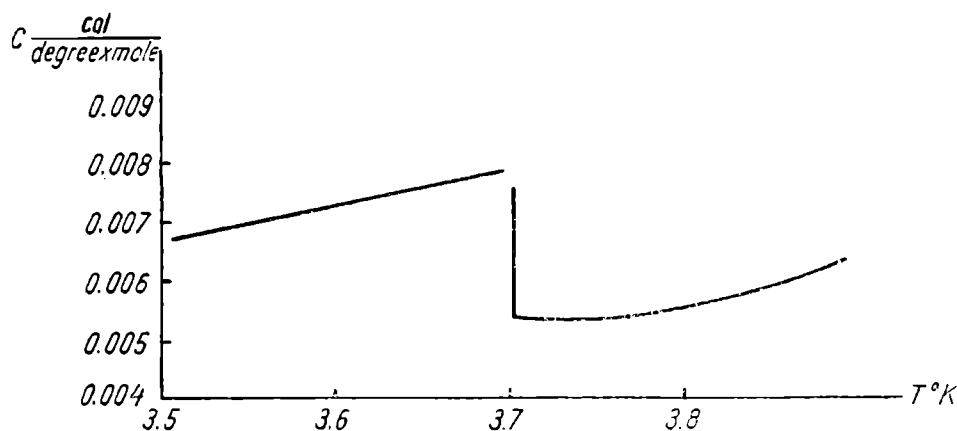


FIG. 32.

curve of the thermal capacity at the transition point, and therefore the presence of λ -curves in phase transitions is no proof of the fact that these transitions are transitions of the second kind.

This conclusion is also shown convincingly by the example of the phase transition of ammonium bromide NH_4Br . At low temperatures anomalies are observed (λ -curves; see Fig. 33) in the temperature behaviour of NH_4Br (as well as in that of NH_4Cl and NH_4I). These pro-

cesses are usually attributed to phase transitions of the second kind on the ground that no release of latent heat is observed. Therefore Ehrenfest's equation (8.7) ought to be valid in this case. On the basis, however, of very accurate measurements of the temperature behaviour of the thermal capacity of NH_4Br it has been shown† that, in reality,

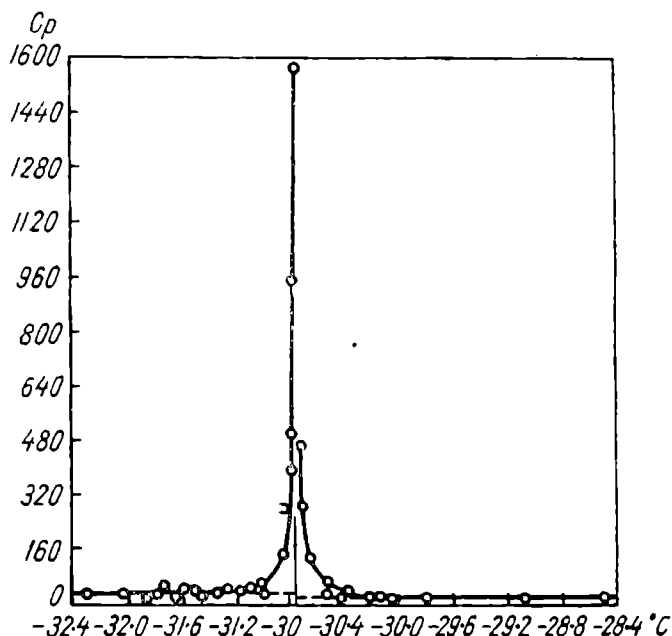


FIG. 33.

the Clapeyron–Clausius equation (8.4) is valid for such transitions, which fact indicates that these transitions belong to the class of phase transitions of the first kind. This is also indicated by the variation of the crystal lattice in such transitions. Though in the s -to- n transitions of NH_4Br , NH_4Cl and NH_4I no (or, more correctly, almost no) heat effect is observed, its presence is revealed by the peak of the thermal capacity at the transition point (λ -curve).

§ 40. The theory of phase transitions of the second kind

After Ehrenfest had introduced, in 1933, the concept of phase transitions of the second kind, their thermodynamic theory was developed in 1937 by Landau. This theory concerns first of all those transitions which are connected with a variation of the symmetry of a body or of the pattern of atoms.

If a transition is accomplished at the temperature T_c , then the phase

† V. Yu. Urbakh; *Zhurnal fizicheskoi khimii* 30, p. 217 (1956).

that is stable for $T < T_c$ is called ordered, and the phase stable for $T > T_c$ is called non-ordered. For a mathematical description of a phase transition of the second kind a certain essentially positive internal parameter† η is introduced, which is called the *ordering parameter*.

The thermodynamic potential Z of a body is therefore a function of T , p and η . In the non-ordered state the parameter η is taken equal to zero. The continuity of the variation of Z in a phase transition of the second kind means that in the vicinity of the transition point η assumes an arbitrarily small value; let us therefore expand $Z(T, p, \eta)$ in the ordered phase in the vicinity of the transition point in a power series with respect to the ordering parameter η

$$Z(T, p, \eta) = Z_0(T, p) + \alpha(T, p) \eta + \frac{1}{2} \beta(p, T) \eta^2 + \dots \quad (8.L)$$

The equilibrium state corresponds to that value of η for which Z has an extremum ($\partial Z / \partial \eta = 0$), which gives

$$\alpha + \beta \eta = 0, \quad (8.M)$$

whence

$$\eta = - \frac{\alpha(p, T)}{\beta(p, T)}. \quad (8.15)$$

This state will be stable if η corresponds to a minimum of Z

$$\frac{\partial^2 Z}{\partial \eta^2} > 0, \quad \text{whence} \quad \beta > 0. \quad (8.N)$$

It follows from (8.15) that, to accord theory with experiment, we need to postulate that for each assigned pressure p there exists a certain temperature T_c such that for $T \geq T_c$ the condition $\alpha(p, T) \equiv 0$ is verified, while for $T < T_c$ then $\alpha(p, T) \neq 0$. In other words, the presence of ordering for $T < T_c$ and its absence for $T \geq T_c$ cannot be derived from the theory but must be introduced in it by proceeding from experimental data.

In the vicinity of the transition point, $\alpha(p, T)$ can be expanded in a power series with respect to $(T - T_c)$

$$\alpha(p, T) = \alpha(p, T_c) + (T - T_c) \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c}, \quad (8.O)$$

† An internal parameter can also be introduced for the characteristic of phase transitions of the first kind. Therefore from the fact that Landau's method can be applied successfully to the analysis of phase transitions of the second kind it does not follow that all processes where this method is applicable are phase transitions of the second kind.

whence

$$\alpha(p, T) = (T - T_c) \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c}, \quad (8.P)$$

since

$$\alpha(p, T_c) = 0. \quad (8.Q)$$

Thus in the vicinity of the transition point the thermodynamic potential Z and the entropy in the ordered state ($T < T_c$) are equal to

$$Z = Z_0 - \frac{\alpha^2}{2\beta} = Z_0 - \frac{(T - T_c)^2}{2\beta} \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c}^2, \quad (8.16)$$

$$S = - \left(\frac{\partial Z}{\partial T} \right)_p = S_0 + \frac{1}{\beta} (T - T_c) \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c}^2, \quad (8.17)$$

where Z_0 and S_0 are the thermodynamic potential Z and the entropy in the non-ordered state.

We obtain from (8.17) that the thermal capacity $C_p = T(\partial S / \partial T)_p$ undergoes a jump at the transition point

$$\Delta C_p = C_p - C_p^{(0)} = \frac{T_c}{\beta} \left(\frac{\partial \alpha}{\partial T} \right)_{T=T_c}^2. \quad (8.18)$$

Since $\beta > 0$, it can be seen from the formula obtained that the thermal capacity of the ordered state proves to be larger than the thermal capacity of the non-ordered state. Such a conclusion of the theory is found to be in agreement with experiment, which can be seen from the data shown for the transition of a conductor to the super-conducting state.

As the functions α and β are single-valued, the solution (8.15) for the equilibrium value of η is also single-valued. This leads to the impossibility of the existence of metastable states: for $T < T_c$ there exists only one ordered phase and the non-ordered phase is absent (unstable); for $T \geq T_c$, on the contrary, only the non-ordered phase is possible but the ordered phase is unstable. In other words, in phase transitions of the second kind neither supercooling nor superheating are possible.

By knowing the jump of thermal capacity, we can easily find also the jumps of other second derivatives of the thermodynamic potential.

Landau's theory is a phenomenological theory, since it cannot determine the form of the functions $\alpha(p, T)$ and $\beta(p, T)$.

By comparing the formula (8.18) of Landau's theory with Ehrenfest's formula (8.11) for the jump of the thermal capacity ΔC_A , we can put $\alpha = A$ and $\beta = -\Delta(\partial \alpha / \partial A)_{T_c}$. Though Landau's theory uses

certain conceptions of a model of matter (ordering, non-ordering etc.), the formula (8.18) of this theory is sometimes even less valuable than Ehrenfest's purely thermodynamic formula (8.11). Thus, in the case of the phase transition of a conductor to the superconducting state we obtain, from Ehrenfest's formula, Rutgers' formula

$$\Delta c = \frac{T}{4\pi} \left(\frac{dH}{dT} \right)_{H=0}, \quad (8.14)$$

which, on the basis of an experimental measurement of $(dH/dT)_T$, gives a quantitative value for the jump of the thermal capacity ΔC . The formula (8.18) cannot give anything similar. Moreover, Rutgers' thermodynamic formula enables us to establish for a given transition the values of α and β in the formula (8.18): $\alpha = H$ and $\beta = 4\pi$. On the whole, however, in the analysis of phase transitions of the second kind Landau's theory is superior to Ehrenfest's purely thermodynamic approach. Thus previous to Landau's work the question of the possibility of supercooling and superheating in phase transitions of the second kind had been incorrectly answered, as a consequence of which contradictions had arisen (see problem no. 14).

§ 41. Critical phenomena

In 1860 D. I. Mendeleev, studying the temperature dependence of surface tension, established that at a certain temperature, called by him the absolute boiling temperature, the difference in the properties of the two coexisting phases, liquid and vapour, vanishes. This state, characterized by determined values of temperature, T_{cr} , pressure, p_{cr} , and volume, V_{cr} , was later called the *critical state*. The equilibrium curve of liquid and vapour on the T, p diagram ends at the critical point.

In 1869 the critical phenomenon was investigated by Andrews and from 1873 onwards, by a group of Kiev physicists under the leadership of M. P. Avenarius.

In 1878 Gibbs developed a general theory of critical phenomena on the basis of his work on the equilibrium and stability of heterogeneous systems. In our exposition of the theory of critical phenomena we shall follow Gibbs.

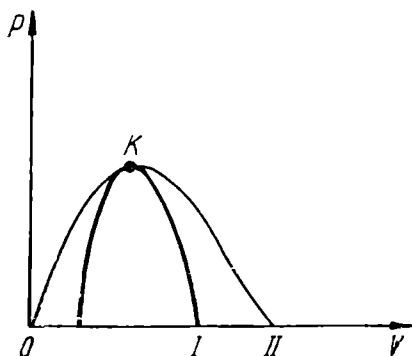


FIG. 34.

1. The theory of critical phenomena according to Gibbs

Under the influence of external actions the state of a phase can vary both continuously (without the arising of a new phase) and discontinuously (with the arising of a new phase). Accordingly there exist two types of boundaries of the region of stability of a phase. These are boundaries of phase stability with respect to (1) continuous and (2) discontinuous variations of state. A boundary of the first type is the set of states of the phase taken by itself, which correspond to the points C of Fig. 24 for various temperatures (the curve I in Fig. 34). A boundary of the second type is the equilibrium curve of phases (Fig. 25 or the curve II in Fig. 34). In the passage through a boundary of stability with respect to discontinuous phase variations, one of the phases becomes relatively more stable than the other, which fact causes a phase transition of the first kind. At a boundary of stability with respect to continuous phase variations the thermodynamic inequalities (6.26), determining the stability of the existence of a phase, assume limit values, namely zero or infinity. As can be seen from Fig. 34, when the stability of a phase with respect to the arising of a new phase fails the stability of the phase with respect to its continuous variations is either retained or fails.

Stable states that lie simultaneously on a boundary of stability both with respect to discontinuous and with respect to continuous phase variations are defined by Gibbs as critical states (the point K in Fig. 34). A *critical phase* is therefore the limit case of the equilibrium of two phases for which the stability conditions are satisfied both with respect to discontinuous and with respect to continuous variations.

Mathematically the boundary of the region of stability of a phase with respect to continuous variations is determined by reducing to equalities the thermodynamic inequalities (6.26), i.e. by the equations

$$\left. \begin{aligned} \left(\frac{\partial T}{\partial S} \right)_{p, A_i, \mu_i} &= 0, & \left(\frac{\partial p}{\partial V} \right)_{T, A_i, \mu_i} &= 0, \\ \left(\frac{\partial A_i}{\partial a_i} \right)_{p, T, \mu_i} &= 0, & \left(\frac{\partial \mu_i}{\partial N_i} \right)_{T, p, A_i} &= 0, \end{aligned} \right\} \quad (8.19)$$

or

$$\left(\frac{\partial X_i}{\partial x_i} \right)_{X_1, \dots, X_{i-1}, X_{i+1}, \dots} = 0, \quad (8.20)$$

where X_i are thermodynamic forces (T, p, H, E, μ, \dots) and x_i are the coordinates associated with them (S, V, M, P, N, \dots). This defini-

tion of the boundary of stability with respect to continuous variations of phase can be written in the following more general form.

When thermodynamic coordinates are taken as independent variables, the differentials of the thermodynamic forces are equal to

$$dX_i = \left(\frac{\partial X_i}{\partial x_1} \right)_{x_2, x_3, \dots, x_n} dx_1 + \left(\frac{\partial X_i}{\partial x_3} \right)_{x_1, x_3, \dots, x_n} dx_3 + \dots \quad (8.R)$$

$$\dots + \left(\frac{\partial X_i}{\partial x_n} \right)_{x_1, \dots, x_{n-1}} dx_n$$

$$(i = 1, 2, \dots, n).$$

The determinant of this system will be

$$D = \begin{vmatrix} \left(\frac{\partial X_1}{\partial x_1} \right)_{x_2, \dots, x_n} & \left(\frac{\partial X_1}{\partial x_2} \right)_{x_1, x_3, \dots, x_n} & \dots & \left(\frac{\partial X_1}{\partial x_n} \right)_{x_1, \dots, x_{n-1}} \\ \vdots & \vdots & \ddots & \vdots \\ \left(\frac{\partial X_n}{\partial x_1} \right)_{x_2, \dots, x_n} & \left(\frac{\partial X_n}{\partial x_2} \right)_{x_1, x_3, \dots, x_n} & \dots & \left(\frac{\partial X_n}{\partial x_n} \right)_{x_1, x_2, \dots, x_{n-1}} \end{vmatrix} = \quad (8.S)$$

$$= \frac{\partial(X_1, X_2, \dots, X_n)}{\partial(x_1, x_2, \dots, x_n)}.$$

In the case of the two independent variables S and V we have

$$D = \begin{vmatrix} \left(\frac{\partial T}{\partial S} \right)_V & \left(\frac{\partial T}{\partial V} \right)_S \\ \left(\frac{\partial p}{\partial S} \right)_V & \left(\frac{\partial p}{\partial V} \right)_S \end{vmatrix} = \frac{\partial(T, p)}{\partial(S, V)} = \frac{\partial(T, p)}{\partial(S, p)} \frac{\partial(S, p)}{\partial(S, V)} = \left(\frac{\partial T}{\partial S} \right)_p D_{11}, \quad (8.T)$$

where $D_{11} = (\partial p / \partial V)_S$ is the minor of the determinant D corresponding to the element of the first column and first row.

In the general case we have, by analogy,

$$D = \left(\frac{\partial X_i}{\partial x_i} \right)_{X_1, X_2, \dots, X_{i-1}, X_{i+1}, \dots} D_{ii} \quad (8.U)$$

and

$$\left(\frac{\partial X_i}{\partial x_i} \right)_{X_1, X_2, \dots, X_{i-1}, X_{i+1}, \dots} = \frac{D}{D_{ii}}. \quad (8.21)$$

Therefore, according to (8.20), the boundary of stability of a phase with respect to continuous variations will be written in the form

$$D = \frac{\partial(X_1, X_2, \dots, X_n)}{\partial(x_1, x_2, \dots, x_n)} = 0. \quad (8.22)$$

Since critical states are stable also with respect to discontinuous variations, then small fluctuation-type variations of the coordinates of a phase for constant thermodynamic forces must not remove the system from the stability boundary (8.22), neither must they lead to the formation of a new phase, i.e. the condition $D = 0$ must be maintained for such fluctuations. This is equivalent to the equality to zero of the derivatives $(\partial D / \partial x_i)_{x_1, x_2, \dots, x_{i-1}, x_{i+1}, \dots}$ and to the inequality $(\partial^2 D / \partial x_i^2)_{x_k} < 0$, which is expressed in the most general form, in the first place, by the equality

$$R = \frac{\partial(D, X_2, \dots, X_n)}{\partial(x_1, x_2, \dots, x_n)} = 0, \quad (8.23)$$

i.e. by equating to zero the determinant of the system (8.20) in which any one of the rows is replaced by a row formed from the coefficients of the linear form

$$dD = \left(\frac{\partial D}{\partial x_1} \right)_{x_2, \dots, x_n} dx_1 + \dots + \left(\frac{\partial D}{\partial x_n} \right)_{x_1, \dots, x_{n-1}} dx_n, \quad (8.V)$$

and, in the second place, by the inequality

$$Q = \frac{\partial(R, X_2, \dots, X_n)}{\partial(x_1, x_2, \dots, x_n)} < 0, \quad (8.24)$$

in which the determinant Q is constructed in the same manner as R .

In the general case the minors of the determinant D and the successive minors of these minors are not equal to zero in the critical state. In the contrary case, for determining the critical state we would have a greater number of independent equations than the number of unknowns, which contradicts the assumption of the existence of a determined critical state. However, the reducing identically to zero of these minors for $x = x_k$ does not add a new independent equation to (8.22) and (8.23), and therefore does not contradict the definition of critical state.

As can be seen from the mathematical definition itself of the boundary of stability of a phase with respect to its continuous and discontinuous variations, the transition through a critical state is only possible between phases of a substance that are described in both these phases by a single equation of state, such as, for example, van der Waals' equation. In this connexion the equation of state, solved with respect to some value of x , is the equation of state for the corresponding phase (for example, liquid and vapour, paramagnetic and ferromagnetic state etc.).

We shall determine the number of degrees of freedom of a critical state from the general formula (6.44)

$$f = k + i - n, \quad (8. W)$$

where k is the number of components and i is the number of thermodynamic forces (T, p, H, E, μ, \dots). By taking into account that in this state we have a single-phase system ($n = 1$), defined additionally by the two limit conditions of stability (8.22) and (8.23), we obtain

$$f_{cr} = k + i - 3. \quad (8. 25)$$

2. The critical point

In the particular case of a simple single-component system characterized, for example, by the coordinates S and V , the number of degrees of freedom $f_{cr} = 0$. This means that the critical state of such a system is only possible for determined values of temperature, pressure and volume, i.e. at a single, critical, point: T_{cr}, p_{cr}, V_{cr} .

The equations of the stability boundary (8.22), (8.23) and (8.24) of the system reduce, at the critical point, to the equations, known from the general course:

$$\left(\frac{\partial p}{\partial V}\right)_{T_{cr}} = 0, \quad \left(\frac{\partial^2 p}{\partial V^2}\right)_{T_{cr}} = 0, \quad \left(\frac{\partial^3 p}{\partial V^3}\right)_{T_{cr}} < 0. \quad (8. 26)$$

In fact, in our case,

$$D = \frac{\partial(p, T)}{\partial(V, S)} = \begin{vmatrix} \left(\frac{\partial p}{\partial V}\right)_S & \left(\frac{\partial p}{\partial S}\right)_V \\ \left(\frac{\partial T}{\partial V}\right)_S & \left(\frac{\partial T}{\partial S}\right)_V \end{vmatrix}, \quad (8. X)$$

$$R = \frac{\partial(D, T)}{\partial(V, S)} = \frac{\partial(D, T)}{\partial(V, T)} \frac{\partial(V, T)}{\partial(V, S)} = \left(\frac{\partial D}{\partial V}\right)_T \left(\frac{\partial T}{\partial S}\right)_V, \quad (8. 27)$$

$$Q = \frac{\partial(R, T)}{\partial(V, S)} = \left(\frac{\partial R}{\partial V}\right)_T \left(\frac{\partial T}{\partial S}\right)_V = \left(\frac{\partial R}{\partial V}\right)_T \frac{T}{C_V}. \quad (8. 28)$$

According to (8.21)

$$\left(\frac{\partial p}{\partial V}\right)_T = -\frac{D}{\left(\frac{\partial T}{\partial S}\right)_V}. \quad (8. 29)$$

None of the elements of the determinant D reduce to zero or infinity at the critical point, since in the contrary case there would be more

equations, independent of (8.22) and (8.23), determining the critical state. Therefore, according to (8.29), the condition $D = 0$ is equivalent to $(\partial p / \partial V)_T = 0$.† It follows from (8.27) that $(\partial D / \partial V)_T = 0$ for $R = 0$. However,

$$\begin{aligned} \left(\frac{\partial D}{\partial V} \right)_T &= \left[\frac{\partial}{\partial V} \left\{ \left(\frac{\partial p}{\partial V} \right)_T \left(\frac{\partial T}{\partial S} \right)_V \right\} \right]_T = \\ &= \left(\frac{\partial^2 p}{\partial V^2} \right)_T \left(\frac{\partial T}{\partial S} \right)_V + \left(\frac{\partial p}{\partial V} \right)_T \left[\frac{\partial}{\partial V} \left(\frac{\partial T}{\partial S} \right)_V \right]_T, \end{aligned} \quad (8.Y)$$

whence for $(\partial p / \partial V) = 0$ and $(\partial D / \partial V)_T = 0$ we obtain $(\partial^2 p / \partial V^2)_T = 0$. Therefore the condition $R = 0$ is equivalent to $(\partial^2 p / \partial V^2)_T = 0$.

From (8.28) we have $(\partial R / \partial V)_T < 0$ for $Q < 0$, since $C_V > 0$ and $T > 0$. However,

$$\left(\frac{\partial R}{\partial V} \right)_T = \left(\frac{\partial^2 D}{\partial V^2} \right)_T \left(\frac{\partial T}{\partial S} \right)_V + \left(\frac{\partial D}{\partial V} \right)_T \left[\frac{\partial}{\partial V} \left(\frac{\partial T}{\partial S} \right)_V \right]_T, \quad (8.Z)$$

whence for $R = 0$ (or $(\partial D / \partial V)_T = 0$) and $(\partial R / \partial V)_T < 0$ we obtain

$$\left(\frac{\partial^2 D}{\partial V^2} \right)_T < 0 \quad (8.AA)$$

or

$$\left(\frac{\partial^3 p}{\partial V^3} \right)_T < 0. \quad (8.AB)$$

Thus the condition $Q < 0$ is equivalent to $\partial^3 p / \partial V^3 < 0$.

In the general case of a single-component system a state of which is determined by the external parameter a and the temperature T , we can, similarly to (8.26), write the conditions for the corresponding critical point (by replacing V by a and p by A). Since, however, each system is characterized always by determined values of pressure and volume, then, by varying pressure in the general case considered, we shall have a whole line of critical states

$$\left(\frac{\partial A}{\partial a} \right)_{p, T_{cr}} = 0, \quad \left(\frac{\partial^2 A}{\partial a^2} \right)_{p, T_{cr}} = 0, \quad \left(\frac{\partial^3 A}{\partial a^3} \right)_{p, T_{cr}} < 0. \quad (8.30)$$

By adding to these equations the equation of state, we can find T_{cr} , A_{cr} and a_{cr} as functions of the pressure p .

† This condition for the critical state follows directly from the definition of the stability boundary of a phase with respect to continuous variations, (8.19). From (8.19) we also obtain that, at the critical point

$$\left(\frac{\partial T}{\partial S} \right)_p = \frac{T}{C_p} = 0 \quad \text{and} \quad C_p = \infty. \quad (8.AC)$$

3. *The passage of a single-component system through a line of critical states*

By assuming that the behaviour of a substance on both sides of the critical-transition line is described by one and the same equation of state, we can expand the thermodynamic potential Z

$$Z(T, p, A) = F(T, V, a) + pV + Aa \quad (8.AD)$$

in a neighbourhood of the critical state in a power series with respect to $(a - a_{cr})$.

Depending on the physical nature of the generalized coordinate, two basic types of transition are possible:

(1) the coordinate a is such that the expansion of the potential Z contains all powers of $(a - a_{cr})$;

(2) the nature of the generalized coordinate a is such that the expansion of Z in the vicinity of the critical state contains only even powers of $(a - a_{cr})$.

M. A. Leontovich, in his book *Introduction to Thermodynamics*, carries out an investigation of the properties of a substance in the vicinity of the critical point T_{cr} , p_{cr} , V_{cr} , when the expansion of the thermodynamic potential of a simple system contains all powers of $\omega = V - V_{cr}$.

Similarly, in an article by I. L. Chubukova† there is considered the behaviour of a single-component system with an additional degree of freedom in the passage through the line of critical states, both for the variation of such thermodynamic coordinate a that the expansion of the potential Z shall contain all powers of $(a - a_{cr})$, and in the case of a coordinate a of a different nature, when such an expansion contains only even powers of $(a - a_{cr})$. Omitting details, which can be found in the article quoted, we shall only show some of its results.

If the nature of the generalized coordinate a is such that all powers of $(a - a_{cr})$ are contained in the expansion of the thermodynamic potential about the transition point, then, for a transition through the line of critical states the volume and the entropy are continuous, while the thermal capacity $C'_{p,A}$ tends to infinity, having a steeper rise for $T' > T_{cr}$ than for $T' < T_{cr}$, when T' tends to T_{cr} (a λ -shaped behaviour of the thermal capacity). In the case of a generalized coordinate of a different nature, when only even powers of $(a - a_{cr})$ are contained in the expansion of Z in the vicinity of the critical state, the volume

† *Vestnik Moskovskogo Universiteta*, No. 6, 117, 1957.

and the entropy are also continuous but the thermal capacity $C_{p, a}$ undergoes a finite jump, the value of which is determined by Ehrenfest's equation (the curve of the temperature behaviour of the thermal capacity does not have the form of a λ -curve).

All this leads to the following conclusions:

(1) Ordinary critical phenomena correspond to such a nature of the generalized coordinate ($a = V$, the volume of the system) when all powers of $(a - a_{cr})$ are contained in the expansion in the vicinity of the transition point. Here the volume and entropy are continuous, but the thermal capacity C_p increases without limits, having a λ -shaped curve.

(2) Phase transitions of the second kind are a particular case of transition through a line of critical states, namely the case when the nature of the generalized coordinate a is such that only even powers of $(a - a_{cr})$ are contained in the expansion of Z in the vicinity of the critical point.

(3) The definition of phase transitions of the second kind as those phenomena for which $\Delta S = 0$ and $\Delta a = 0$ is not, in a certain sense, complete; we also need to add that in such transitions the jumps of the thermal capacity and of the other second derivatives of the thermodynamic potential are *finite*; when these, however, are infinite, we have ordinary critical phenomena.† If we do not complete, in such a manner, the definition of phase transitions of the second kind, then there is no difference whatsoever between phase transitions of the second kind and ordinary critical phenomena.

As can be seen from the analysis of critical phenomena according to Gibbs, the unity of these two classes of phenomena consists in that both represent stable states that lie on the stability boundary with respect to both discontinuous and continuous phase variations.

PROBLEMS

110. By assuming the transition heat, λ , to be a constant quantity, show that the saturated-vapour pressure varies with a variation of temperature according to an exponential law.

111. The melting point of I_2 is equal to 114°C . The increase of vapour tension in the vicinity of the melting point for an increase of the melting temperature by 1° is equal to 4.34 mmHg/degree. Find the sublimation heat of iodine at the melting temperature: the vapour tension of solid iodine at this temperature is equal to 88.88 mm Hg.

112. Under which pressure will water boil at 95°C ? The latent heat of vaporization of water is 539 cal/g.

† In the He-I to He-II transition the behaviour of the thermal capacity has a λ -shaped curve, and therefore this phenomenon is not a phase transition of the second kind but an ordinary critical phenomenon.

113. The curve of the critical field can often be represented to a sufficient accuracy by a parabola

$$H_c(T) = H_0 \left[1 - \left(\frac{T}{T_c} \right)^2 \right]. \quad (8. AE)$$

By using this expression, find the difference of the values of the specific entropies and of the specific thermal capacities in the n - and s -states.

114. It is known that a substance is found in the state at which its thermodynamic potential Z is a minimum. If we represent on a graph the temperature dependence of the Z of two phases (at $p = \text{const}$), the point of intersection, T_0 , of the two curves will be the point of phase transition: passing through T_0 the substance is represented by a point on the curve that corresponds to smaller values of Z . For phase transitions

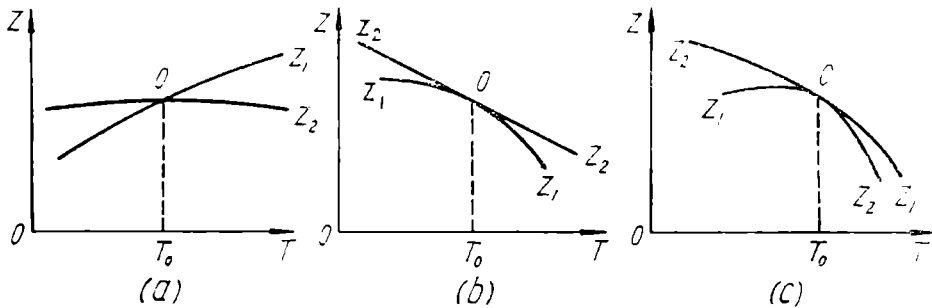


FIG. 35.

of the first kind the intersection of the Z_1 and Z_2 curves is represented in Fig. 35 *a*. In phase transitions of the second kind the tangents to the two curves at the transition point coincide (since the entropy is expressed by the derivative of the thermodynamic potential with respect to temperature). In the case of simple contact of the two curves (Fig. 35 *b*) no transition can occur since both for $T < T_0$ and $T > T_0$ the substance would be found all the time in one and the same phase. Therefore at a transition point there occurs the contact of the two curves and their intersection (Fig. 35 *c*), which leads to the equality not only of the first but also of the second derivatives of the thermodynamic potential, i.e. the entropy and the thermal capacity. But this corresponds to phase transitions not of the second but of the third kind. Therefore phase transitions of the second kind are impossible. Which statement contains the error of this result due to Jüsti and Laue?

115. Verify using the example of a van der Waals' gas that the compressibility $(\partial V / \partial p)_T$ and the coefficient of thermal expansion $(\partial V / \partial T)_p$ become infinite at the critical point.

CHAPTER IX

NERNST'S HEAT THEOREM

AT THE beginning of the twentieth century (in 1906) a new proposition, called Nernst's heat theorem, was added to the two laws of thermodynamics.

Nernst's theorem does not follow from the first and second law, but expresses a new natural law, and therefore it is often referred to as the third law of thermodynamics. Today it can be derived from the basic propositions of quantum statistics.

Historically, however, Nernst's theorem emerged, before the inception of quantum mechanics, from the needs of thermodynamics on the basis of extensive experimental thermodynamic investigations. Therefore we shall establish it here by proceeding from Nernst's work, and shall obtain by its means a series of fundamental thermodynamic corollaries.

§ 42. Nernst's theorem

Historically, Nernst's theorem was established in connexion with the problem of chemical affinity. Its significance, however, is wider than the solution of only this problem.

By chemical affinity we mean the ability of substances of reacting chemically with each other; therefore chemical affinity determines the action of the chemical forces of reacting substances. The solution of the problem of chemical affinity consisted in finding a quantitative measure of this affinity. The initial solution of this problem was suggested by Thomsen and Berthelot. Since, as is well-known, in many cases of chemical reactions heat is evolved, Thomsen and Berthelot enunciated the principle that the quantity of heat released in a reaction is a measure of the chemical affinity: the greater the heat evolved in the reaction of certain substances the larger the affinity between them.

In spite of the apparent plausibility of the Thomsen-Berthelot principle, this cannot, however, be assumed as a solution of the problem

of chemical affinity. The fact is that, together with exothermal reactions, there also exist endothermal reactions in which heat is not evolved but is absorbed. According to Thomsen and Berthelot this would correspond to a negative chemical affinity, which is meaningless.

A correct solution of the problem of chemical affinity was firstly given by van't Hoff. He showed that chemical affinity must be measured not according to the heat effect, i.e. not according to the decrease of internal energy ΔU of the reacting bodies, but according to the decrease of free energy ΔF of these bodies at constant values of temperature and volume,[†] since the decrease of free energy under these conditions is equal to simply the work of the chemical forces: $\Delta F = W$.

We have for this work, which is a measure of affinity, the Gibbs-Helmholtz equation

$$W = Q + T \left(\frac{\partial W}{\partial T} \right)_v. \quad (9.1)$$

In integrating (9.1) there arises, as is known (see page 96) the constant I which is thermodynamically indeterminate, and therefore the absolute value of affinity, W , cannot be found. The overcoming of this difficulty led to the establishing of Nernst's theorem.

Analogous difficulties had also been encountered in determining the absolute value of entropy. The second law defines the entropy by means of the differential equation

$$dS = \frac{\delta Q}{T} \quad (9.A)$$

and therefore leaves the entropy constant S_0 indeterminate. At the same time a whole series of physical quantities, such as the constant of chemical equilibrium, the saturated vapour pressure in a liquid-vapour two-phase system etc., depend on the value of S_0 .

The theoretical evaluation of this constant and of the absolute value of chemical affinity became possible after Nernst, relying on ample experimental data accumulated in the study of the behaviour of substances at low temperatures, had established that the difference $W - Q$ or $\Delta F - \Delta U = T(\partial \Delta F / \partial T)_v$ is always small and, as temperature decreases to the absolute zero, it decreases more rapidly than according to a linear law. This means that in the product $T(\partial \Delta F / \partial T)_v$ the factor $(\partial \Delta F / \partial T)_v$ tends to zero as T tends to zero.

[†] Or else, according to the decrease of the thermodynamic potential, ΔZ , if a reaction occurs with constant values of temperature and pressure.

Thus, in quasi-static isothermal processes in equilibrium systems at temperatures tending to the absolute zero, the variation of free energy $F_2 - F_1$ ceases to be temperature dependent, i.e.

$$\frac{\partial}{\partial T} (F_2 - F_1)_{T \rightarrow 0} \rightarrow 0 \quad (9.B)$$

or

$$\lim_{T \rightarrow 0} \frac{\partial}{\partial T} (\Delta F) = 0. \quad (9.2)$$

This experimental fact bears the name of *Nernst's heat theorem*.

From the Gibbs-Helmholtz equation we obtain now that

$$W = Q \quad \text{for } T \rightarrow 0 \quad (9.C)$$

or

$$\Delta F = \Delta U \quad \text{for } T \rightarrow 0. \quad (9.D)$$

Graphs of the temperature dependence of ΔU and ΔF have, thus, the form shown in Fig. 36. The tangent to these curves at the $T = 0$ point is parallel to the T axis in accordance with (9.2).

Nernst's theorem (9.2) can also be represented in another form. Since $(\partial F / \partial T)_V = -S$, then from (9.2) we obtain

$$S_2 - S_1 \rightarrow 0 \quad \text{for } T \rightarrow 0 \quad (9.E)$$

or

$$\lim_{T \rightarrow 0} \Delta S = 0, \quad (9.3)$$

i.e. for $T \rightarrow 0$ isothermal processes occur without variation of entropy. This means that for $T \rightarrow 0$ the entropy ceases to be a function of state; it approaches a constant value independent of the parameters of state:

$$\lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial p} \right)_T = \lim_{T \rightarrow 0} \left(\frac{\partial S}{\partial V} \right)_T = 0. \quad (9.4)$$

For $T \rightarrow 0$ the entropy of a system cannot be varied by any action whatsoever. Therefore Nernst's theorem can be formulated thus: *the zero-temperature isothermal coincides with an adiabatic*.

Planck qualified Nernst's theorem by imposing an additional condition to entropy. He assumed that for $T \rightarrow 0$ not only does ΔS tend to zero but the entropy itself $S \rightarrow 0$: *the zero-temperature isothermal*

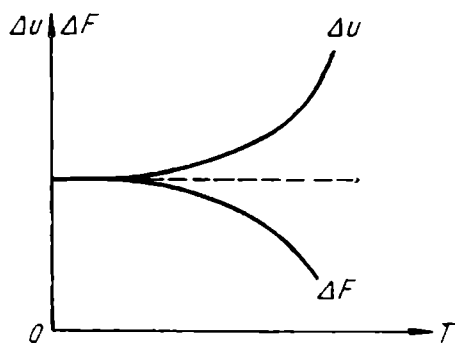


FIG. 36.

coincides with the zero-entropy adiabatic. (Nernst's theorem or the third law of thermodynamics.)

The equality to zero of the entropy for $T \rightarrow 0$ is connected with the quantum nature of real systems. At the absolute zero an equilibrium system is found in a fully determined unique state with minimum energy E_0 . The thermodynamic probability of such a state, W , is equal to unity. Therefore, according to Boltzmann's formula

$$S = k \ln W \quad (9.F)$$

we obtain that for $T = 0$ the entropy $S = 0$.

Measurements show that for a series of substances (alloys, all amorphous bodies, the chemical compounds CO, NO etc.) the entropy does not tend to zero, for $T \rightarrow 0$, but to a finite positive value. This does not, however, indicate a restriction to Nernst's theorem but points out the fact that the substances indicated are not found in an equilibrium state; processes at low temperatures in alloys and other bodies proceed very slowly and the system we are dealing with, for which the value of entropy is determined in practice, is a system in a non-equilibrium state.

The expressions for the entropy of an ideal gas and a van der Waals' gas do not obey the condition $S \rightarrow 0$ for $T \rightarrow 0$, since the corresponding equations of state, by means of which these expressions are obtained, are inapplicable to gases at low temperatures. From this there follow far-reaching results on the degeneracy of gases at low temperatures.

There are today no grounds for assuming that the validity of Nernst's theorem is restricted to certain condensed media only; it is accepted to be valid for all substances.

§ 43. Corollaries of Nernst's theorem

From Nernst's theorem we can deduce a whole series of important corollaries concerning the properties of substances for $T \rightarrow 0$ and the determination of the entropic and chemical constants. Let us consider some of them.

1. *The behaviour of thermal coefficients for $T \rightarrow 0$*

By definition the thermal coefficient of expansion α and the thermal coefficient of pressure γ are equal to

$$\alpha = \frac{1}{V_0} \left(\frac{\partial V}{\partial T} \right)_p, \quad \gamma = \frac{1}{p_0} \left(\frac{\partial p}{\partial T} \right)_v. \quad (9.G)$$

From $dZ = -SdT + Vdp$ and $dF = -SdT - pdV$ we have

$$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T \quad \text{and} \quad \left(\frac{\partial p}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T, \quad (9.H)$$

and therefore

$$\alpha = -\frac{1}{V_0} \left(\frac{\partial S}{\partial p}\right)_T \quad \text{and} \quad \gamma = \frac{1}{p_0} \left(\frac{\partial S}{\partial V}\right)_T. \quad (9.J)$$

According to Nernst's theorem the entropy does not vary for $T \rightarrow 0$ (it does not depend on the parameters of state p and V), and therefore for $T \rightarrow 0$

$$\alpha \rightarrow 0 \quad \text{and} \quad \gamma \rightarrow 0, \quad (9.5)$$

i.e. the coefficient of thermal expansion and the thermal coefficient of pressure reduce to zero for $T \rightarrow 0$.

2. The calculation of entropy and the behaviour of the thermal capacities C_p and C_v for $T \rightarrow 0$

Nernst's theorem makes the evaluation of all thermodynamic functions extremely simple. Before this theorem had been established, in order to evaluate the entropy one had to know the temperature dependence of the thermal capacity and the thermic equation of state.

According, however, to Nernst's theorem the entropy can be found by knowing only the temperature dependence of the thermal capacity but without having available the thermic equation of state, which is unknown for condensed bodies. In fact, from the definition of thermal capacities

$$C_v = T \left(\frac{\partial S}{\partial T}\right)_v \quad \text{and} \quad C_p = T \left(\frac{\partial S}{\partial T}\right)_p \quad (9.K)$$

we obtain, by using Nernst's theorem,

$$S = \int_0^T \frac{C_v dT}{T} \quad \text{and} \quad S = \int_0^T \frac{C_p dT}{T}. \quad (9.6)$$

Thus the very important problem of evaluating the entropy reduces to determining only the temperature dependence of the thermal capacity. This explains the fact that the "problem of the thermal capacity" has occupied such an important place in the physics of the beginning of the twentieth century. The solution of this problem was taken up by Einstein, Debye, Born, Cramers and others.

It follows from the formula (9.6) that for $T' \rightarrow 0$ the thermal capacities C_p and C_v must tend to zero, since in the contrary case the integrals would diverge logarithmically at their lower limit. In fact, let us suppose the contrary to be true, i.e. that for $T' \rightarrow 0$ the thermal capacity C_v does not tend to zero. Then the expansion of C_v in a power series must contain a constant term, i.e.

$$C_v = a + bT + \dots \quad (9.7)$$

On substituting (9.7) in (9.6) we shall obtain

$$S = a \ln T \Big|_0^{T'} + bT + \dots, \quad (9.L)$$

whence it follows that at whatever temperature $T' \neq 0$ the entropy $S \rightarrow -\infty$, but this contradicts Nernst's theorem which assumes the finiteness of entropy at all finite temperatures including the limit case $T' = 0$. Therefore $C_v \rightarrow 0$ for $T \rightarrow 0$; similarly also $C_p \rightarrow 0$ for $T \rightarrow 0$. As can be seen, this result does not require Nernst's theorem in all its contents: it is obtained merely from the assumption that for $T = 0$ the entropy is finite.

3. The unattainability of the absolute zero temperature

A consequence of Nernst's theorem is the unattainability of the absolute zero temperature. In fact let us consider a Carnot cycle with $T_1 = T'$ heater temperature and $T_2 = 0$ refrigerator temperature (Fig. 37).

According to the second law we have for a cycle $\oint \delta Q/T = 0$ or

$$\Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0. \quad (9.M)$$

But $\Delta S_{12} = Q/T$, $\Delta S_{23} = 0$ (adiabatic process), $\Delta S_{34} = 0$ (according to Nernst's theorem), and $\Delta S_{41} = 0$ (adiabatic process). Therefore $Q/T = 0$ although $Q \neq 0$.

This contradiction points out the fact that it is impossible to descend on the zero-temperature isothermal!

The absolute zero temperature cannot be reached!†

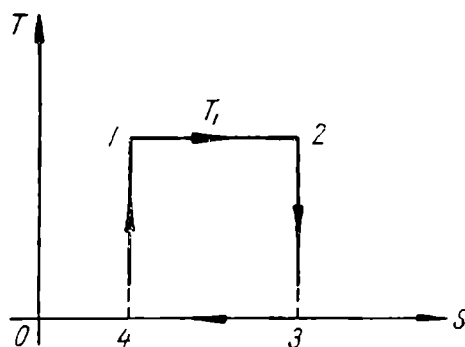


FIG. 37.

† Often only this consequence of Nernst's theorem is called the third law of thermodynamics of the unattainability of the absolute zero.

4. *The degeneracy of an ideal gas*

The expression for the entropy of a classical ideal gas

$$S = C_V \ln T + R \ln V + S_0, \quad (9.N)$$

obtained from Clapeyron's equation $pV = RT$, does not satisfy Nernst's theorem, since for $T \rightarrow 0$ it does not lead to $S \rightarrow 0$ but to $S \rightarrow -\infty$. This indicates the fact that at low temperatures an ideal gas must not behave according to Clapeyron's equation but otherwise. Such a departure of an ideal gas from the classical gas laws (obtained from classical statistics) is called *degeneracy*.

Therefore Nernst's theorem predicts the degeneracy of ideal gases at low temperatures.

As developments of quantum statistics show, such a degeneracy does actually occur, although at very low temperatures (the degeneracy temperature of Bose's ideal gas is equal to 1°K).

5. *Evaluation of the entropic constant S_0 for a gas*

Nernst's theorem can be indirectly used for finding the entropic constant of an ideal gas. In fact, let us consider a solid body in equilibrium with [its] gas. In this connexion their chemical potentials must be the same

$$\mu_1 = \mu_2. \quad (9.O)$$

However, $\mu = u - Ts + pv$, and therefore the chemical potential of the gas is equal to

$$\mu_1 = u_1 - T(c_p \ln T - R \ln p + s_0) + pv_1, \quad (9.P)$$

while the chemical potential of the solid body is

$$\mu_2 = u_2 - Ts_2 + pv_2 \quad (9.Q)$$

and therefore

$$RT \ln p = [u_2 - u_1 + p(v_2 - v_1)] + c_p T \ln T - Ts_2 + Ts_0. \quad (9.R)$$

We have for the solid body, according to Nernst's theorem

$$s_2 = \int_0^T \frac{c_p}{T} dT, \quad (9.S)$$

and the expression in square brackets above represents the sublimation heat Q ; therefore

$$s_0 = -\frac{Q}{T} - c_p \ln T + \int_0^T \frac{c_p}{T} dT + R \ln p. \quad (9.T)$$

By determining experimentally the quantities Q , c_p , p and T we can evaluate the entropic constant s_0 for the gas.

PROBLEMS

116. By using Nernst's theorem show that the thermodynamically indeterminate constant I (see page 96) is equal to zero.

117. Show that for $T \rightarrow 0$ the surface tension and the e.m.f. of a cell do not depend on temperature.

118. As experiment shows, the internal energy (the heat effect) in the transformation of rhombic to monoclinic sulphur, varies with temperature according to the law

$$Q = Q_0 + \beta T^2 = 50.4 + 3.69 \times 10^{-4} T^2. \quad (9.U)$$

Determine the affinity with which rhombic sulphur is transformed at a temperature T to monoclinic sulphur, and the transformation temperature.

119. Two vessels connected by a capillary are filled with He-II. If a temperature difference $\Delta T = T_2 - T_1$ is generated in the vessels, this causes in them a pressure difference (a difference of levels) $\Delta p = p_2 - p_1$. Explain this phenomenon and establish the relation between ΔT and Δp by using the fact that He-II behaves as a mixture of two liquids: a "superfluid" one having no viscosity or entropy and therefore having, according to Nernst's theorem, the temperature $T = 0$, and another a "normal" one behaving as an ordinary liquid.

NEGATIVE ABSOLUTE TEMPERATURES

§ 44. The possibility of the existence of states with a negative absolute temperature

IN § 14, by proceeding from the second law of thermodynamics we have established that the ratio of the absolute temperatures T_1 and T_2 of two states of an arbitrary system is expressed by the exponential function

$$\frac{T_1}{T_2} = e^{\int_{t_1}^{t_2} \frac{\left(\frac{\partial A}{\partial t}\right)_a dt}{\left(\frac{\partial U}{\partial a}\right)_{t^{+A}}}}. \quad (10.1)$$

From this the conclusion is usually drawn that the absolute temperature cannot change its sign, so that it can be assumed to be always positive (or always negative).

Such a conclusion, however, goes beyond the actual contents of the relation (10.1). This relation was obtained in the analysis of quasi-static processes and establishes that the absolute temperature T cannot vary its sign in the quasi-static transition from one equilibrium state to another. Therefore it leaves open the question of the sign variation of T if a system passes from one equilibrium state to another by non-static means. To conclude from the expression (10.1) that the sign of the absolute temperature T is constant would only be legitimate if the expression (10.1) were qualified by the additional statement that states which can be reached from a given one non-statically can always be reached from it quasi-statically also. As experiment shows, this statement is true in all cases of ordinary systems, the ones encountered most often of all. Therefore for such systems the absolute temperature cannot vary its sign and it can be assumed to be always positive (or always negative). However, from the single relation (10.1) without the above additional statement it does not follow that negative absolute temperatures cannot exist together with positive ones.

The possibility of the existence of negative absolute temperatures cannot be denied either by proceeding from Nernst's theorem. In fact the unattainability of the absolute zero temperature leads only to the impossibility of a transition through it from positive to negative absolute temperatures, but does not exclude the possibility of the existence of negative absolute temperatures (alongside with positive absolute temperatures).

States with negative absolute temperatures are not only possible but they do exist in reality. Numerous experiments on nuclear magnetic resonance were carried out in 1951 in order to generate states with

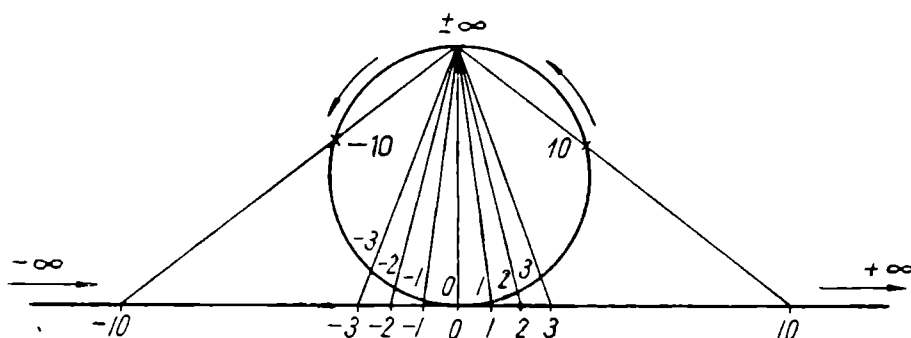


FIG. 38.

negative absolute temperatures. The conditions for the existence of a system at negative absolute temperatures are, as we shall see below, so rigid, that such systems are rarely encountered by us in practice, except certain systems of nuclear spins.

Negative absolute temperatures are attained not by abstracting from a system all the energy of thermal motion but, on the contrary, by communicating to the system a greater energy than that corresponding to infinite temperature. To do this is impossible in the majority of bodies, since the internal energy in them is infinite at indefinitely high temperatures. Such systems cannot be found in states with negative absolute temperature, if for them a positive absolute temperature has already been chosen. In certain systems, however, as the temperature increases to ∞ , the internal energy approaches asymptotically a finite limit value, and this gives the possibility of obtaining in them states with negative absolute temperature when greater energy than this given limit value is communicated to the system. A system in such states, by having greater energy than the energy at infinite temperature, has an "ultra-infinite" temperature. In mathematics, however, there is no "ultra-infinity" on the numerical straight line, but there is

only an indefinitely far removed point, and if we cross this point, we shall approach 0°K from the negative side (see Fig. 38: by proceeding to the right away from zero along the numerical axis, on leaving $+\infty$ we shall move from $-\infty$ to zero. The numerical axis can be projected onto the numerical circle where the highest point of the circle corresponds to the indefinitely far removed point of the axis. By contouring the circle anticlockwise we shall describe the whole numerical axis). Thus at negative absolute temperatures a system is not colder than the absolute zero ($+0^\circ\text{K}$) but is hotter than at infinite temperature ($\pm\infty^\circ\text{K}$). In other words the region of negative absolute temperatures does not lie "below the absolute zero" but "above the infinite temperature". Therefore negative absolute temperatures are higher than positive ones. In the direction of its increase, temperature passes on the scale through the following successive values

$$+0^\circ\text{K}, \dots, +500^\circ\text{K}, \dots, +1000^\circ\text{K}, \dots, -500^\circ\text{K}, \dots, -0^\circ\text{K}. \quad (10.2)$$

The $+1000^\circ\text{K}$ temperature is intermediate between $+500^\circ\text{K}$ and -500°K . The artificiality of the above construction of the T scale is a fortuitous result of the arbitrary choice of the usual temperature function. If the temperature function had been chosen in the form $-1/T$, then the lowest temperatures would correspond to $-\infty$ for this function, infinite temperature of the usual T scale would correspond to zero, and negative absolute temperature of the [usual] T scale would correspond to positive values of this function. For such a temperature function the algebraic order and the order from smaller to larger temperature would be identical. The function $-1/T$ is often used in thermodynamics in investigating the properties of systems in the absolute zero region, since it enables us to "expand" the temperature scale at low temperatures. It can be seen from what has been expounded that for the purposes of negative temperatures the $-1/T$ scale is in many respects more convenient than the T scale.

§ 45. A system with negative absolute temperature

The following simple model shows how negative absolute temperatures are realized in practice.

Let us have a system of "elementary magnets" (for example, electronic, atomic or nuclear magnetic moments). At low temperatures these magnets settle in a strong magnetic field in the manner shown in Fig. 39*a*, i.e. they reach a state with minimum energy. When energy

is communicated to the system of magnets (when temperature is increased) the magnets are no longer all directed along the field, and as more energy is received by the system the more disordered the distribution of the magnets will be. At a certain instant conditions are

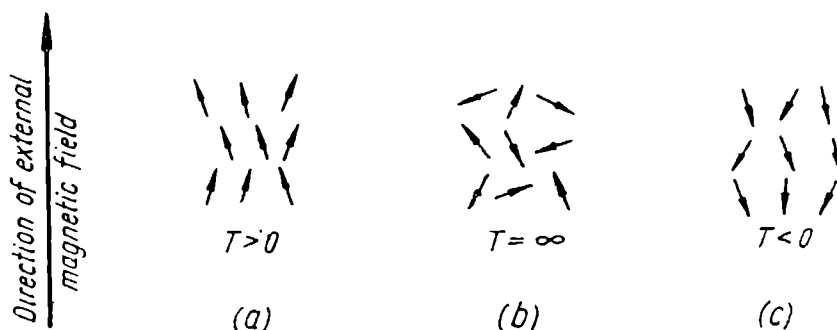


FIG. 39.

reached when disorder becomes complete—the system has completely lost its magnetization. This corresponds to $T = +\infty$ (Fig. 39b). By continuing to communicate energy to the system we can attain a state when the elementary magnets are orientated in the opposite direction to the field (Fig. 39c). In this state the internal energy of the system is larger than at an indefinitely large temperature, and therefore the system has a negative absolute temperature.

We can now formulate the basic condition that a system must satisfy in order that it may be found in a state with negative absolute temperature: *the energy of the thermodynamic system must have a finite limit value for $T \rightarrow \infty$.*

Of course, the system must be thermally insulated from any other systems that do not satisfy the basic condition, i.e. the time needed to establish thermodynamic equilibrium in the system must be small in comparison with the time needed for an appreciable quantity of energy to be lost or acquired from other systems.

The temperature dependence of the internal energy of a system capable of being found in states with a negative absolute temperature is shown in Fig. 40 (E_{lim} is the limit value of energy for $T = \infty^\circ\text{K}$).

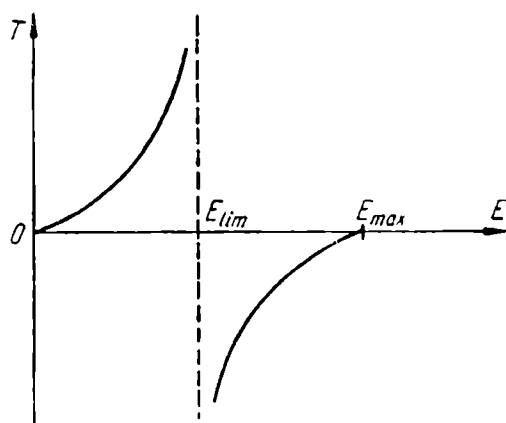


FIG. 40.

The majority of systems do not satisfy the above indicated requirements, as a consequence of which systems with negative absolute temperatures are rarely encountered. The system of nuclear spins in certain crystals satisfies these conditions. The thermodynamic equilibrium in such a system is established by nuclear spin-spin interaction. This spin-spin process of the establishing of thermodynamic equilibrium is characterized by the relaxation time T_2 which is of the order of 10^{-5} sec. The interaction of the spin system with the lattice is characterized by a relaxation time T_1 , which amounts to many minutes, i.e. is considerably larger than T_2 . In the thermodynamics of spin systems the interaction with the lattice corresponds to leakage of heat through the walls of the system. The considerable difference of the times T_1 and T_2 leads to the fact that the system of spins, after reaching internal thermodynamic equilibrium, still remains for a relatively large time practically insulated from the lattice. We can say that for the duration of this time the spin system is in thermodynamic equilibrium.

A system with a negative absolute temperature was first realized in practice by Purcell and Pound in 1951[†] as a result of experiments to study the properties of systems of nuclear spins in very pure crystals of lithium fluoride LiF. In these crystals the time T_1 of spin-lattice relaxation at room temperature is of the order of 5 min, while the time T_2 of spin-spin relaxation is approximately equal to the period of Larmor's precession of a nuclear magnetic moment in an external magnetic field, the value of which is smaller than 10^{-5} sec.

In an external magnetic field the energy of a system of nuclear spins has a finite limit for $T \rightarrow \infty$.

Thus in a system of nuclear spins of LiF in a magnetic field all conditions are satisfied for the existence of states with negative absolute temperature. In order that this system be moved from states with positive absolute temperature to states with negative absolute temperature, we need to obtain that the nuclear magnetic moments be directed against the field. Purcell and Pound have done this in the following manner.

A pure crystal of LiF is introduced into an intense magnetic field (6376 oersted), as a result of which the polarization of the nuclear magnetic moments occurs—they are orientated along the field. Then this crystal is rapidly transferred, through the Earth's magnetic field, into a small solenoid with 100 oersted field intensity, generated by a

[†] E. M. Purcell and R. V. Pound; *The Physical Review* 81, 279 (1951).

constant magnet and directed parallel to the strong field. Next, by means of the discharge of a capacitor of $2 \mu\text{F}$ capacitance charged to 8000 V a current of great intensity is obtained in the turns of the solenoid, which in 0.2μ sec changes the magnetic field from $+100$ oersted to -100 oersted. This "inverted" magnetic field will take 1 msec to return to the initial value, i.e. a considerably longer time than the spin-spin relaxation time T_2 . Finally the crystal, passing through the Earth's magnetic field, is rapidly returned to the intense magnetic field (6376 oersted) in which the polarization of the nuclei is measured by the method of nuclear magnetic resonance. The whole operation from the instant of removing the crystal from the intense field to its return to this field was carried out in 2–3 seconds i.e. in a considerably shorter time than the time T_1 of spin-lattice relaxation. The reverse polarization of the nuclei was revealed by measurements. This indicates that the variation of direction of the magnetic field during the discharge of the capacitor, occurring in a time of 0.2μ sec comparable with the period of Larmor's nuclear precession and with the time T_2 of spin-spin relaxation, has led to the turning of the magnetic moments, so that after this the system of spins was found to be in a thermodynamic-equilibrium state with negative absolute temperature. This state was retained for about 5 min, after which as a consequence of spin-lattice interaction the system returned to a state with positive temperature.†

Today the "reduction" of a spin-system to a state with negative absolute temperature is achieved by means of the so-called 180-degree high-frequency pulse which, by acting on the sample for a period of time Δt comparable with T_2 rotates the macroscopic magnetic moment by 180° .

It can be seen from what has been expounded that the transition of a system from positive absolute temperatures to negative absolute temperatures is in principle non-static, since the variation of external parameter (the external field) that leads to such a transition occurs in a time comparable with the relaxation time T_2 . It can also be seen that cases are possible for non-ordinary systems when states that are reached from a given one by non-static means cannot be reached from it quasi-statically.

† Details of the interpretation of the Purcell and Pound work and a discussion of the whole problem of negative absolute temperatures can be found in the article by A. Abraham and U. Proctor "Spin temperature" (in the collection *Problemy sovremennoi fiziki*, No.1, 1959).

§ 46. The thermodynamics of systems at negative absolute temperatures

1. Systems at negative absolute temperatures have a series of new specific properties which ordinary systems have not. In order to establish these properties we shall, by relying on experiment, formulate at first the basic laws of thermodynamics for such systems.

The thermodynamic concepts “work”, “heat”, “quantity of heat”, “hotter body” are used in the analysis of states with negative absolute temperature in the same meaning as in the case of states with positive absolute temperatures. This means that the formulation of the first law of thermodynamics for negative absolute temperatures remains unvaried

$$\delta Q = dU + \delta W. \quad (10.3)$$

Without modification also remains the formulation of the second law of thermodynamics in the form of the law of the existence and increasing of entropy, while other formulations of the second law are modified. In order to establish this we shall take, as the initial expression of the second law, one that follows directly from experiment on the conversion of heat into work and work into heat.

We have observed in Chapter III that the second law of thermodynamics establishes, in the first place, a general law of the conversion of heat into work and expresses, in the second place, specific laws of this conversion and of the conversion of work into heat both in the case of ordinary and in the case of non-ordinary systems. The general law of the conversion of heat into work in both cases of systems consists in that, when such a conversion occurs in a closed-cycle process, a portion of heat is always ceded by the *working body* to other bodies. As has been shown in § 13, this (first) element of compensation, which in the case of ordinary systems coincides with the second element of compensation (a variation of the thermodynamic state of other bodies) leads to the existence of entropy in an equilibrium system. Hence it follows that in Carathéodory's form the second law does not vary: in the vicinity of each state of an arbitrary thermally homogeneous system such states exist that can be reached from it by adiabatic means. This means that in every equilibrium system in a state with negative absolute temperature (just as in the case of ordinary systems) there exists entropy as a function of the state of the system

$$dS = \frac{\delta Q}{T}. \quad (10.4)$$

The specific law of the conversion of heat into work and work into heat in the case of ordinary systems consists, as is known, in the fact that while for the conversion of heat into work in a closed-cycle process there occurs a variation of the thermodynamic state of other bodies, on the contrary the conversion of work into heat is not connected with such a variation:

$$\underset{\rightarrow}{Q} > \underset{\rightarrow}{W} \quad \text{and} \quad \underset{\rightarrow}{W} = \underset{\rightarrow}{Q}. \quad (10.5)$$

As experiment shows,† in the case of non-ordinary systems, when they are found in states with $T < 0$, the specific law of the direct and inverse conversions of heat into work consists in that heat is converted into work without any variations whatsoever in the surrounding bodies while it is impossible to convert entirely work into heat in a closed process without variation in the surrounding bodies:‡

$$\underset{\rightarrow}{Q} = \underset{\rightarrow}{W} \quad \text{and} \quad \underset{\rightarrow}{W} > \underset{\rightarrow}{Q}. \quad (10.6)$$

Therefore we can formulate the second law for non-ordinary systems for $T < 0$ in the following form: *a perpetual motor of the second kind is impossible and this statement admits of a converse proposition.*

This means that in a closed-cycle process for $T < 0$ neither can heat be converted into work without compensation (we have in mind the first element of compensation) nor can work be converted into heat without compensation (we have in mind the second element of compensation).

Thus, for all systems (ordinary and non-ordinary) we can proceed from the following formulation of the second law: *a perpetual motor of the second kind is impossible and this statement does not admit of a converse proposition in the case of ordinary systems and does admit of a converse proposition for $T < 0$ for non-ordinary systems.*

The concepts of “reversible” and “irreversible” processes are defined in the case of negative absolute temperatures by the fact whether their reverse processes are connected or not with a non-compensated conversion of work into heat. Thus the process of the transition of a system from a state 1 to a state 2 is called reversible if the reverse process from 2 to 1 is not connected with a non-compensated conversion of

† We have in mind experiments on nuclear magnetic resonance which we cannot describe here.

‡ The conversions of heat into work and work into heat are therefore complementary: when one is possible without variations in other bodies the other is impossible and vice versa.

work into heat; on the contrary, the process of the transition of a system from 1 to 2 is called irreversible if the reverse transition from 2 to 1 is connected with a non-compensated conversion of work into heat.

The definitions of “quasi-static” and “non-static” processes remain without modification.

In § 16 from the relations (3.1) or (10.5) we had obtained from non-static processes in ordinary systems

$$T dS > dU + \delta W \quad (10.7)$$

and

$$dS > 0 \quad (10.8)$$

in the case of an adiabatically-insulated system.

Similarly, from the relations (10.6) which represent the second law

of thermodynamics for non-ordinary systems for $T < 0$, we can find an analytical expression of this law for non-static processes in such systems. To do this we shall consider two equilibrium states, close to each other, 1 and 2 of a certain non-ordinary system (at negative absolute temperatures).

Let a quantity of heat δQ_{n-st} be communicated to the system in a non-static transition from 1 to 2 (Fig. 41) and let the system accomplish the work δW_{n-st} ; then by the first law

$$\delta Q_{n-st} = dU + \delta W_{n-st}. \quad (10.9)$$

If, however, the system passes from the state 1 to the state 2 quasi-statically, then the quantity of heat received by it from the thermostat will be equal to δQ and the work accomplished δW so that

$$\delta Q = dU + \delta W. \quad (10.10)$$

By subtracting the equation (10.10) from the equation (10.9) we shall obtain

$$\delta Q_{n-st} - \delta Q = \delta W_{n-st} - \delta W = R. \quad (10.11)$$

The quantity R is different from zero, since in the opposite case this would mean that the irreversible process 1-2 can be carried out in the reverse direction without compensation; the quantity R cannot be negative, since in the opposite case this would mean that after a cycle external work has gone into heating a thermostat without any varia-

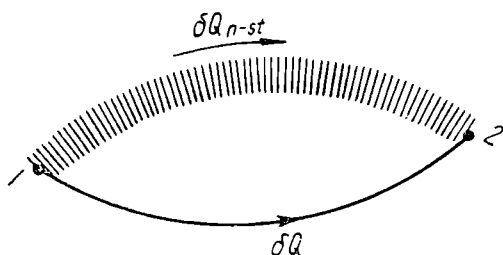


FIG. 41.

tion whatsoever in other bodies which, according to (10.6) is impossible; the quantity R can be positive since this corresponds to work over a cycle at the expense of heat of a thermostat which, according to (10.6) is possible. Thus

$$\delta Q_{n-st} > \delta Q \quad \text{and} \quad \delta W_{n-st} > \delta W, \quad (10.A)$$

and, since $\delta Q = TdS$, then

$$T dS < \delta Q_{n-st}. \quad (10.B)$$

In adiabatic non-static processes when $\delta Q_{n-st} = 0$ we obtain ($T < 0$)

$$dS > 0, \quad (10.C)$$

which expresses the law of the increase of entropy in non-static processes in isolated systems with negative absolute temperature. It can be seen from what has been expounded that the law of the existence and increase of entropy (the second law) is valid both in the case of ordinary and in the case of non-ordinary systems.

The basic equation of thermodynamics for systems at negative absolute temperatures has the form

$$T dS \leq dU + \delta W, \quad (10.12)$$

where the equality corresponds to equilibrium and the inequality to non-equilibrium processes.

The various formulations of the third law of thermodynamics remain unmodified at negative absolute temperatures if by absolute zero temperature we mean both the absolute zero of positive temperature and that of negative temperature. The temperatures $+0^\circ\text{K}$ and -0°K correspond to completely different physical states. For the first a system is found in the state with minimum possible energy, and for the second in the state with maximum possible energy. A system cannot become colder than $+0^\circ\text{K}$ since energy can no longer be abstracted from it. It cannot become hotter than -0°K since it can no longer absorb energy. The unattainability principle will be formulated in the following manner: it is impossible by means of whatever arbitrarily idealized procedure comprising a finite number of operations, to cool any system down to the absolute zero of positive temperature, or to heat any system up to the absolute zero of negative temperature.

The specific thermal capacity vanishes both at $+0^\circ\text{K}$ and at -0°K . The physical reason for this consists in that both at $+0^\circ\text{K}$ and at -0°K all elements of a system reach in the end their energy states of minimum or maximum energy, and heat can no longer be abstracted or absorbed

respectively. The specific thermal capacities at $\pm\infty^\circ\text{K}$ (these two temperatures are physically identical since they correspond to equal values of all thermodynamic quantities) also vanish but for a different reason: the very large temperature variations of a system for a small variation of its internal energy as the system approaches $\pm\infty^\circ\text{K}$.

2. Let us now consider certain properties of systems in states with a negative absolute temperature.

(a) It follows from the equation (10.4) that in communicating heat ($\delta Q > 0$) to a system, its entropy does not increase, as at positive absolute temperatures, but decreases—the system passes to a more ordered state.

(b) By means of the fundamental equation of thermodynamics (10.12) we can establish the direction in which heat flows in the thermal contact of two bodies of different temperature.

Let us have two bodies at negative absolute temperatures T_1 and T_2 . Let us bring them in thermal contact. Let, in this connexion, the quantity of heat δQ flow from the first to the second body. Then, since the heat-transmission process is irreversible for a finite temperature difference, we have

$$-\frac{\delta Q}{T_1} + \frac{\delta Q}{T_2} > 0, \quad (10.D)$$

whence $T_1 > T_2$, i.e., according to the temperature scale (10.2), heat flows spontaneously from the hot to the cold body. (We say that the first body is hotter than the second, if heat needs to be communicated to the second body (without variation of external parameters) for it to be found in equilibrium with the first body when in thermal contact with it.)

It is also easy to verify that in the thermal contact of systems with absolute temperatures of different signs heat flows from the body with negative absolute temperature to the body with positive temperature, i.e. again from the hot to the cold body.

(c) At negative absolute temperatures various closed-cycle processes, similar to Carnot's magnetic cycle, can be carried out.

Let, as is usual, the temperature of the hot reservoir be T_1 and that of the cold reservoir T_2 . Then the efficiency of Carnot's cycle is equal to

$$\eta = 1 - \frac{T_2}{T_1}. \quad (10.E)$$

Since the temperature of the hot reservoir is larger than the tempera-

ture of the cold reservoir then $T_1 > T_2$, $|T_1| < |T_2|$, $T_2/T_1 > 1$ and therefore $\eta < 0$. This means that at negative absolute temperatures work must be expended in order to abstract heat from a hot body and transmit it to a cold one. In this connexion, according to the first law, the heat communicated to the cold body is larger than that abstracted from the hot one by the value of the work accomplished. When such an engine acts in the opposite direction, i.e. performs the role of a refrigerating machine, then by the transfer of heat from the cold body to the hot one work is produced by it. If then, by means of the thermal contact of the two bodies, heat is allowed to flow from the hot to the cold body, we shall obtain a periodically working engine which, without causing any variations in the surrounding medium, accomplishes work at the expense of a single (cold!) body. As we see, in the region of negative absolute temperatures it is possible to implement the Thomson-Planck perpetual motor of the second kind.

The efficiency of a Carnot cycle working between negative temperatures is smaller than unity, just as in the region of positive temperatures. This means that both at positive and negative absolute temperatures heat engines absorb more heat energy than they produce work.

To accomplish a (reversible) Carnot cycle between temperatures of different signs is impossible. The fact is that, using the adiabatic magnetization of a system of spins, we can raise the temperature as high as we like on the positive temperature scale, but we cannot make it pass to negative values; a similar statement is valid if the initial state has a negative absolute temperature. As has been shown in the previous section the passage of a system from positive to negative absolute temperatures can only be accomplished by means of a non-static process.

(d) The adiabatic demagnetization of a spin system at negative absolute temperatures heats the system, instead of cooling it as would be the case at positive temperatures.

(e) The ease with which heat is converted into work leads to important practical applications of systems with negative absolute temperature.

At negative absolute temperatures the majority of resistances are negative, and therefore systems at such temperatures are amplifiers: an electromagnetic wave passing through a system at a negative absolute temperature is not absorbed but amplified. This is apparently, of very great importance for the future of radiolocation and other branches of physics.

§ 47. Stability of the state of a system at negative absolute temperature

Let us, in concluding, clarify the problem of whether states of a system at negative absolute temperatures are stable. To do this, similarly to §§ 30, 31 we shall proceed from the fundamental equation (10.12) of the thermodynamics of systems with negative temperatures. From (10.12) we obtain for non-static processes in such systems

$$T dS < dU + p dV, \quad (10.13)$$

whence it follows that in isolated systems ($U = \text{const}$, $V = \text{const}$) with $T < 0$ equilibrium occurs for a maximum of entropy.

Thus the general condition for the equilibrium of an isolated system at negative absolute temperatures is that the entropy of the system be a maximum (just as in the case of positive absolute temperatures)

$$\Delta S < 0 \quad \text{or} \quad \delta S = 0, \quad \delta^2 S < 0. \quad (10.14)$$

In order to find the general condition for equilibrium at $T < 0$ for a system in a thermostat with constant volume or constant pressure, we shall pass in (10.13) to the corresponding independent variables. Then we shall obtain

$$dF > -S dT - p dV \quad (10.15)$$

and

$$dZ > -S dT + V dp. \quad (10.16)$$

It can be seen from (10.15) that in isothermal-isochoric non-static processes in a system with $T < 0$ the free energy increases and is a maximum at equilibrium. The general equilibrium condition can be written, therefore, in this case in the form

$$\Delta F < 0 \quad \text{or} \quad \delta F = 0, \quad \delta^2 F < 0. \quad (10.17)$$

Similarly, from (10.16) we obtain the general equilibrium condition of a system in a thermostat ($T < 0$) at constant pressure

$$\Delta Z < 0 \quad \text{or} \quad \delta Z = 0, \quad \delta^2 Z < 0. \quad (10.18)$$

The condition for equilibrium stability of such a system is determined either directly from the general condition $\Delta Z < 0$ or from the condition $\delta^2 Z < 0$. From the condition $\Delta Z < 0$ we find, similarly to (6.25),

$$\Delta T \Delta S - \Delta p \Delta V < 0, \quad (10.19)$$

whence

$$\left(\frac{\partial T}{\partial S} \right)_p = \frac{T}{C_p} < 0 \quad \text{or} \quad \left(\frac{\partial p}{\partial V} \right)_T < 0 \quad (10.F)$$

or

$$C_p > 0 \quad \text{or} \quad \left(\frac{\partial p}{\partial V} \right)_T < 0. \quad (10.20)$$

Similarly, from the condition $\delta^2 Z < 0$, by using the expression for $\delta^2 Z$ for virtual variations of S and V (found in the solution of problem no. 96)

$$\delta^2 Z = \frac{\partial^2 U}{\partial S^2} \delta S^2 + 2 \frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} \delta V^2, \quad (10.G)$$

we obtain the stability condition of our system

$$\frac{\partial^2 U}{\partial S^2} \delta S^2 + 2 \frac{\partial^2 U}{\partial S \partial V} \delta S \delta V + \frac{\partial^2 U}{\partial V^2} \delta V^2 < 0, \quad (10.H)$$

which will be satisfied for arbitrary values of δS and δV if

$$\frac{\partial^2 U}{\partial S^2} < 0 \quad \text{or} \quad \frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 < 0. \quad (10.21)$$

The first of these inequalities gives $\partial^2 U / \partial S^2 = T / C_v < 0$ and, since $T < 0$,

$$C_v > 0, \quad (10.22)$$

i.e. the thermal capacity at constant volume must be positive. The second condition (10.21) reduces to the form (see the solution of problem no. 96)

$$\frac{\partial^2 U}{\partial S^2} \frac{\partial^2 U}{\partial V^2} - \left(\frac{\partial^2 U}{\partial S \partial V} \right)^2 = - \frac{T}{C_v} \left(\frac{\partial p}{\partial V} \right)_T < 0, \quad (10.J)$$

which gives

$$\left(\frac{\partial p}{\partial V} \right)_T < 0. \quad (10.23)$$

Thus the conditions for equilibrium stability of states of a system with negative absolute temperatures are the same as at positive absolute temperatures, and are expressed either in the form (10.20) or in the form

$$C_v > 0 \quad \text{or} \quad \left(\frac{\partial p}{\partial V} \right)_T < 0. \quad (10.24)$$

By choosing, in thermodynamics, the internal energy to be a monotonically increasing function of temperature (which is always possible, see problem no. 1) the thermal capacity C_v is always positive, and therefore states with negative absolute temperature are stable.

CHAPTER XI

FUNDAMENTALS OF THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES

THE POWER of thermodynamics consists in that it enables us to establish general laws for quasi-static processes without finding out their molecular mechanism; this makes it necessary to consider it as a separate, relatively independent part of molecular physics.

In the analysis of non-static processes, classical thermodynamics indicates only their direction, but does not enable us to obtain quantitative results. Classical thermodynamics is not concerned with the theory of irreversible processes. As these have today great practical interest, the construction of a thermodynamics of irreversible processes is a natural aim.

Such a macroscopic theory of irreversible processes has been created in the last two decades.

In this chapter we shall expound the basic propositions of this theory and shall consider some of its applications.

§ 43. The fundamental propositions of the thermodynamics of irreversible processes

1. A great number of irreversible processes are known, the laws of which are expressed phenomenologically by linear relations between cause and effect. For example, the law of thermal conductivity stating the proportionality of the heat flow to the temperature gradient ($I = -\kappa \text{ grad } T$, $\kappa > 0$), the law of diffusion stating the proportionality of the flow of a component of a mixture to the concentration gradient ($j = -D \text{ grad } c$, $D > 0$), Ohm's law stating the proportionality of current density to the potential gradient ($j = -\sigma \text{ grad } \varphi$), Newton's law stating the proportionality of the force of internal friction to the velocity gradient ($F = -\eta \text{ grad } u$) etc.

If two or more such phenomena occur at the same time, by superimposing on each other, they cause the arising of a new effect. For

example, the superposition of thermal conductivity and electric conductivity gives rise to thermoelectricity, the superposition of diffusion and thermal conductivity gives rise to thermodiffusion etc. Mathematically these effects are described by adding additional terms in the corresponding phenomenological relationships; for example, in the case of thermodiffusion we have

$$j = -D \text{ grad } c - \kappa \text{ grad } T, \quad (11.A)$$

i.e. in thermal diffusion the flow of matter arises both under the action of the concentration gradient and under the action of a temperature gradient.

The reasons that cause irreversible phenomena are referred to, in the thermodynamics of such phenomena, as forces and are denoted X_i ($i = 1, 2, \dots$; temperature gradient, concentration gradient, chemical affinity etc.). The quantitative characteristics of the corresponding irreversible phenomena caused by the forces X_i are called flows I_i ($i = 1, 2, \dots$; heat flow, diffusion flow, the quantity of chemically reacting substances etc.). Physically these quantities are usually rates of variation of corresponding parameters of state.

2. All the above-mentioned laws have been obtained from experiment (phenomenological laws) and not from a unified theory of irreversible processes as might be built up by proceeding from general conceptions on these processes.

In principle the most complete and far-reaching theories of irreversible processes are statistical or kinetic theories, which reveal the molecular nature of these processes and permit a quantitative determination of the coefficients (κ , D , σ , η , etc.) occurring in the phenomenological laws. Such theories, however, are based on certain molecular models and are applicable only for determined classes of irreversible processes. Therefore, in spite of their superiority from the physical viewpoint, they have not led to the development of a macroscopical theory of irreversible processes.

The thermodynamics of irreversible processes which has been constructed in recent years is a generalization of classical thermodynamics and of the linear laws of certain irreversible processes.

The generalization of classical thermodynamics is based first of all on the concept of local equilibrium. It is known that the relaxation time increases with an increase of the dimensions of the system. Therefore individual macroscopically-small parts of a system themselves reach an equilibrium state considerably earlier than the establishing

of equilibrium between these small parts. Owing to this, although the system as a whole is not found in equilibrium, we can speak, all the same, of local equilibrium in macroscopically-small parts of the system, by characterizing these parts by determined values of temperature, chemical potential and other thermodynamic quantities. Such a use of thermodynamic parameters assumes, in the first place, that small parts of the system, though small from the macroscopical viewpoint (i.e. of considerably smaller dimensions than those of the system itself), do still contain a large number of particles and that, in the second place, the deviations from equilibrium of the system are small.

A rigorous criterion as to which deviations may be considered small can be established only in a statistical approach to the problem. Such calculations determine, clearly, quantitative limits of applicability of the thermodynamics of irreversible processes. It is found that in the case of a gas we can consider such deviations to be small, for which the variation of temperature (and of other parameters of state) over a mean free-path length is much smaller than the value of temperature itself (or of the other corresponding parameter), while the variations of velocities must be small in comparison with the mean velocity of thermal motion of the molecules (or the velocity of sound)†.

By generalizing classical thermodynamics, the thermodynamics of irreversible processes:

(1) applies to parts of a system in local equilibrium the fundamental equation of thermodynamics for quasi-static processes

$$T dS = dU + \delta W - \sum_i \mu_i dN_i, \quad (11.1)$$

where S , U and W are referred here to a single particle or to unit volume, while μ_i denotes the chemical potential of the i -th component of the system;

(2) assumes that the entropy, under equilibrium conditions as well, depends explicitly only on the thermodynamic parameters T , U and μ and, only in terms of these, does it as well depend on time and coordinates.

(3) assumes that the total variation of entropy of a system is obtained by adding up the entropy variations in the individual parts.

† Under normal conditions the mean free-path length is of the order of 10^{-4} cm. Therefore the limits of applicability of the theory are still very wide in practice. Having assessed these limits for gases, we have justification for assuming that also in other cases there exists a wide region of applicability of the thermodynamics of irreversible processes.

In addition to such a generalization of classical thermodynamics, the thermodynamics of irreversible processes also generalizes in two directions the linear-proportionality laws of certain irreversible phenomena. These generalizations add to the equation (1.1) two more fundamental principles of the thermodynamics of irreversible processes—the *linear law* and *Onsager's reciprocity relations*.

According to the *linear law* the flow I_i caused by the action of forces X_k is proportional to these forces

$$I_i = \sum_{k=1}^n L_{ik} X_k \quad (i = 1, 2, \dots, n). \quad (11.2)$$

The coefficients L_{ik} are called *phenomenological (kinetic) coefficients*; in this connexion L_{ii} is, for example, the coefficient of thermal conductivity, the diffusion coefficient, electric conductivity etc., while the coefficients L_{ik} are connected with superposing phenomena (for example, the thermal-diffusion coefficient etc.).

Onsager's reciprocity relations establish that for a suitable choice of the flows I_i and forces X_i the matrix of the kinetic coefficients is symmetrical, i.e.

$$L_{ik} = L_{ki} \quad (i, k = 1, 2, \dots, n). \quad (11.3)$$

These relations establish a connexion between two superposing phenomena in a stationary state (for example, between thermal diffusion—a temperature gradient causes a concentration gradient—and the effect opposite to it—a concentration gradient gives rise to a temperature gradient).

The choice of the corresponding flows and forces is carried out by proceeding from the fundamental equation of the thermodynamics of irreversible processes which determines the rate of increase of entropy

$$\dot{S} = \sum_i I_i X_i. \quad (11.4)$$

This equation, called the *equation of the "rise of entropy"*, is established in the following manner.

Let us consider an adiabatically insulated system, the state of which is characterized by parameters a_1, a_2, \dots, a_n (pressure, concentration, temperature etc.). Let the equilibrium values of these parameters be equal to $a_1^0, a_2^0, \dots, a_n^0$. We shall determine the state of a non-equilibrium system by the deviations of the parameters a_i from their equilibrium values, i.e. by the quantities $\alpha_i = a_i - a_i^0$ ($i = 1, 2, \dots, n$). In an equilibrium state S is a maximum and the values of all para-

meters α_i are equal to zero. In a non-equilibrium state the deviation of entropy from its equilibrium value will be negative and, in the first approximation, we can write it in the form

$$\Delta S = S - S_0 = -\frac{1}{2} \sum_{i,k} g_{ik} \alpha_i \alpha_k, \quad (11.5)$$

where $||g_{ik}||$ is a positively definite matrix.

As we have already said, the flows I_i are rates of variation of the parameters of state α_i

$$I_i = \dot{\alpha}_i \quad (i = 1, 2, \dots, n), \quad (11.B)$$

while the forces X_i , as the causes of the increase of entropy for a variation of the parameters α_i , are determined by the equations

$$X_i = \frac{\partial(\Delta S)}{\partial \alpha_i} = - \sum_{k=1}^n g_{ik} \alpha_k. \quad (11.6)$$

From (11.5) and (11.6) we obtain the fundamental equation (11.4)

$$\dot{S} = - \sum_{i,k} g_{ik} \dot{\alpha}_i \alpha_k = \sum_i I_i X_i. \quad (11.4)$$

The thermodynamic theory of any one irreversible process consists in finding the associated flows I_i and forces X_i from the equation (11.4) by determining \dot{S} and subsequently using the equations (11.2) and (11.3).

Both the linear law (11.2) and Onsager's reciprocity relations (11.3) can be justified statistically, but in the thermodynamics of irreversible processes they are considered as new principles which are generalizations of experimental data.

A proof of the symmetry of the kinetic coefficients with respect to the indices i and k is based on the microscopic reversibility (i.e. on the invariance of elementary laws with respect to variation of the sign of time), the theory of fluctuations and the fact that the attenuations of fluctuations obey the ordinary macroscopic laws for irreversible processes.

3. In concluding this section we shall determine the rate of local increase of entropy in the case of the thermal conduction process in a homogeneous isotropic solid body.

Let us consider a certain volume in a body not uniformly heated, and let us determine in it the balance of energy and entropy. The internal

energy of unit mass is a function of the coordinates and time $U(x, y, z, t)$. Let the heat-flow density be I .

The volume variation of the individual volume considered, due to thermal expansion and accompanying expenditure of energy, will be neglected by us. The flow of particles in the case of a solid body will also be excluded. We have, therefore, from (11.1)

$$dU = T dS, \quad (11.7)$$

and by the law of conservation of energy

$$\varrho \frac{\partial U}{\partial t} = - \operatorname{div} I, \quad (11.C)$$

or

$$\varrho \frac{\partial U}{\partial t} + \operatorname{div} I = 0, \quad (11.8)$$

where ϱ is the density of the substance. From (11.7) and (11.8) we obtain

$$\varrho \frac{\partial S}{\partial t} + \frac{1}{T} \operatorname{div} I = 0, \quad (11.D)$$

or

$$\varrho \frac{\partial S}{\partial t} + \operatorname{div} \frac{I}{T} = - \frac{1}{T^2} (I, \operatorname{grad} T), \quad (11.9)$$

since

$$\operatorname{div} \frac{I}{T} \equiv \frac{1}{T} \operatorname{div} I + \left(I, \operatorname{grad} \frac{1}{T} \right) = \frac{1}{T} \operatorname{div} I + \frac{1}{T^2} (I, \operatorname{grad} T) \quad (11.E)$$

The equation (11.9) can be written in the form

$$\varrho \frac{\partial S}{\partial t} + \operatorname{div} S = \theta, \quad (11.10)$$

where $S = I/T$ is the entropy-flow density, while $\theta = -(I, \operatorname{grad} T)/T^2$ is the local increment of entropy per unit time. Since, according to the second law, heat does not flow spontaneously from a cold to a hot body, then the scalar product $(I, \operatorname{grad} T)$ is negative and therefore $\theta > 0$. We shall arrive at the same result if we use (11.2):

$$\theta = - \frac{1}{T^2} (I, \operatorname{grad} T) = \frac{\kappa}{T^2} (\operatorname{grad} T)^2, \quad (11.11)$$

which is always positive (since $\kappa > 0$). Vice versa, if we assume, in accordance with the second law, $\theta > 0$, we can obtain from (11.11) $\kappa > 0$.

The expression for the local increment of entropy (11.11) can be rewritten in the form

$$\theta = \frac{1}{T} (I, K) = \frac{1}{T} (I_x K_x + I_y K_y + I_z K_z) \quad (11.F)$$

or

$$\theta = \frac{1}{T} \sum_i I_i K_i. \quad (11.12)$$

We obtain, by comparing (11.12) with (11.4), that the coefficients K_i are proportional to the thermodynamic forces: $K_i = T X_i$.

§ 49. Thermoelectrical phenomena

Three thermoelectrical phenomena in isotropic bodies are known experimentally: 1) the thermoelectric effect, (2) Peltier's effect and (3) Thomson's effect. The essence of these phenomena consists respectively in the following:

(1) at the junction of two different conductors of different temperature there arises a thermo-e. m. f.;

(2) when electric current flows in a thermally homogeneous system through the junction of two different conductors, a quantity of heat proportional to the intensity of current is either released or absorbed at the junction (Peltier's heat);

(3) when electric current flows in a thermally inhomogeneous system, additional heat which is proportional to the temperature gradient and to the intensity of current (Thomson's heat) is released in it together with Joule's heat.

The problem consists in developing a theory of these phenomena by proceeding from the fundamental propositions of the thermodynamics of irreversible processes.

To this end, similarly to the treatment of the case of thermal conductivity, we shall find the local increment of entropy θ in an inhomogeneous conductor when current flows and a temperature gradient is present in it.

Let current of density j be carried by charges $-e$ ($e > 0$) under the action of an electric field $E = -\text{grad}\varphi$ (φ is the electric potential). The variation of volume of the isolated part of metal considered, connected with the passage of current will be neglected by us.

In the presence of an electric field equilibrium occurs, as we know (see problem no. 94), not when the chemical potentials μ are equal but when the electrochemical potentials $\mu = \mu - e\varphi$ are equal.

If μ is referred to 1 mole of moving charged particles, then dN will determine the number of moles of these particles entering the given volume of metal, and the equation (11.1) will in our case have the form

$$T dS = dU - (\mu - F\varphi) dN, \quad (11.13)$$

where $F = eN_0$ is the absolute value of the charge of a mole of electrons (Faraday's number) which is equal to 96,500 coulombs (N_0 is Avogadro's number), so that $\mu/F = \mu/eN_0 = \xi/e$ ($\xi = \mu/N_0$ is the chemical potential referred to one electron).[†] From (11.13) we obtain

$$\frac{\partial S}{\partial t} = \frac{1}{T} \frac{\partial U}{\partial t} - \frac{1}{T} (\mu - F\varphi) \frac{\partial N}{\partial t}. \quad (11.14)$$

The derivative $\partial N/\partial t$ occurring here will be found from the law of conservation of charge, and the derivative $\partial U/\partial t$ from the law of conservation of energy. On substituting them in (11.14) we shall find an expression for θ .

The number of carriers of charge in 1 g of metal is equal to N_0N , where N is the number of moles of moving charges in 1 g. If the electron mass density (i.e. the mass of electrons in 1 cm³ of metal) is equal to ρ , then the quantity $-\rho N_0Ne$ is the charge of unit volume, and therefore by the law of conservation of charge we have

$$-\frac{\partial}{\partial t} (-\rho N_0Ne) = \text{div } j, \quad (11.G)$$

whence

$$\rho \frac{\partial N}{\partial t} = \frac{1}{F} \text{div } j. \quad (11.15)$$

As current flows, each unit of volume, on the one hand, loses energy owing to heat flow I (this loss is equal to $-\text{div } I$) and, on the other hand, receives per unit time, in the first place, electrical energy (j, E) and, in the second place, additional potential energy $\varphi \partial(-\rho N_0Ne)/\partial t = -\varphi \text{div } j$ as a result of the increase of charge of the unit volume. Thus, by the law of conservation of energy we have

$$\rho \frac{\partial U}{\partial t} = -\text{div } I + (j, E) - \varphi \text{div } j. \quad (11.16)$$

[†] The quantity $-\text{grad } (\xi/e)$ is the equilibrium contact field caused by the inhomogeneity of the conductor but not connected with the rising of current (see (11.23)).

By substituting (11.15) and (11.16) in (11.14) we shall obtain

$$\begin{aligned} e \frac{\partial S}{\partial t} + \operatorname{div} \frac{1}{T} \left[I + \frac{\xi}{e} j \right] = \\ = \frac{1}{T} \left\{ \left(I, -\frac{1}{T} \operatorname{grad} T \right) + \left(j, E + T \operatorname{grad} \frac{\xi}{eT} \right) \right\}. \end{aligned} \quad (11.17)$$

This equation shows that a variation of entropy at a given place can occur both on account of inflow of entropy from without and on account of irreversible processes occurring inside the given volume. The equation can be rewritten in the form

$$e \frac{\partial S}{\partial t} + \operatorname{div} S = \theta, \quad (11.18)$$

where $S = [I + j\xi/e]/T$ is the density of entropy flow and θ is the local increment of entropy per unit time, equal to

$$\theta = \frac{1}{T} \left\{ \left(I, -\frac{1}{T} \operatorname{grad} T \right) + \left(j, E + \operatorname{grad} \frac{\xi}{e} \right) \right\}. \quad (11.19)$$

In agreement with (11.4) and (11.12) the expression (11.19) for θ is of the form

$$\theta = \frac{1}{T} \sum_i I_i K_i. \quad (11.H)$$

i.e. is a linear function of the flows I and j . These same flows, according to the linear law (11.2), are linear functions of the coefficients qualifying them in (11.19), and are therefore equal to

$$\left. \begin{aligned} I &= -L_{11} \frac{1}{T} \operatorname{grad} T + L_{12} \left(E + \operatorname{grad} \frac{\xi}{e} \right), \\ j &= -L_{21} \frac{1}{T} \operatorname{grad} T + L_{22} \left(E + T \operatorname{grad} \frac{\xi}{eT} \right). \end{aligned} \right\} \quad (11.20)$$

According to (11.3) we have

$$L_{12} = L_{21}. \quad (11.21)$$

By solving the equations (11.20) with respect to I and E we obtain

$$I = -\kappa \operatorname{grad} T - \Pi j, \quad (11.22)$$

$$E = \frac{1}{\sigma} j - \alpha \operatorname{grad} T - \operatorname{grad} \frac{\xi}{e}, \quad (11.23)$$

where the coefficients κ , Π , α and $1/\sigma$ are expressed in terms of L_{11} ,

L_{12} , L_{21} and L_{22} , and their meaning is easily established from an analysis of (11.22) and (11.23).

In fact, from (11.22) in the absence of current in the conductor we obtain $I = -\kappa \text{ grad } T$, whence it is seen that κ is *the coefficient of thermal conductivity*; from (11.23) in the absence of a temperature gradient in a homogeneous conductor we have $j = \sigma E$, and therefore σ is *the coefficient of electric conductivity*. If in a conductor $j = 0$, then (11.23) shows that in such a conductor there exists a field E due to $\text{grad } T$ and $\text{grad } \xi$: $E = -\alpha \text{ grad } T - \text{grad } (\xi/e)$. The coefficient α is called *the thermoelectric motive force* (thermo-e. m. f.). If $\text{grad } T = 0$, then according to (11.22) the heat flow $I \neq 0$ and has the value Πj ; this flow is caused by the transport of charge. The quantity Π is called *the Peltier coefficient* which, as we shall see, is connected with the Peltier effect.

As a consequence of the reciprocity relation (11.21) we obtain the following relation connecting the coefficient Π and α

$$\Pi = \alpha T. \quad (11.24)$$

This relation was firstly obtained by a completely different method by Thomson, and is referred to as *Thomson's second relation*. We can see that it is the expression of a particular case of Onsager's principle.

Let us now consider the thermoelectric phenomena on the basis of the equations obtained.

(1) Let us imagine an open circuit made up of two different conductors of different temperature. According to (11.23) between these conductors there arises, in addition to the contact potential difference, also a thermo-e. m. f. which depends on the physical nature of the conductors (α) and their temperature

$$\varphi_{T_2} - \varphi_{T_1} = \int_1^2 \alpha dT. \quad (11.J)$$

If such a circuit is closed and the temperatures of the two junctions are equal to T_1 and T_2 , a thermo-e. m. f. arises in the circuit, equal to

$$\oint (E, dl) = \oint \alpha dT = \int_1^2 \alpha_2 dT + \int_2^1 \alpha_1 dT = \int_{T_1}^{T_2} (\alpha_2 - \alpha_1) dT, \quad (11.K)$$

and, for a small temperature difference

$$\oint (E, dl) = \int_{T_1}^{T_2} (\alpha_2 - \alpha_1) dT \approx (\alpha_2 - \alpha_1) (T_2 - T_1). \quad (11.L)$$

From this it can be seen that in a closed circuit a thermo-e. m. f. is possible only in the case of different temperature of the junctions.

The arising of a thermo-e. m. f. is due to the redistribution of carriers of current resulting from the temperature gradient.

(2) Let us consider a thermally homogeneous system of conductors through which the current j flows. In the case of two different conductors 1 and 2 (of 1 cm^2 cross-section) we have that, at the place of the junction, the energy $\Pi_1 j$ per second arrives in the direction of the current along the first conductor, and the energy $\Pi_2 j$ leaves along the second conductor. Therefore the energy $(\Pi_2 - \Pi_1)j$ is released in the form of heat at the junction of such conductors. This phenomenon is known under the name of *Peltier's effect*. We obtain, in agreement with experiment, that Peltier's heat is proportional to the intensity of current.

(3) Let us take now a thermally inhomogeneous system with current, and let us find the variation of energy $q \partial U / \partial t$ per unit time in a unit volume of such a chemically homogeneous system. According to the equation (11.16), by substituting in it the expressions for I and E from (11.22) and (11.23) in the case of a constant current or of a slowly varying current (when $\text{div } j = 0$), we obtain

$$q \frac{\partial U}{\partial t} = \text{div} (\kappa \text{ grad } T) + \frac{j^2}{\sigma} + \left(\frac{\partial \Pi}{\partial T} - \alpha \right) (j, \text{grad } T). \quad (11.25)$$

We see from this expression that the variation of energy in a thermally inhomogeneous system is caused by thermal conductivity $\text{div}(\kappa \text{ grad } T)$, by release of Joule's heat j^2/σ and by the combined action of thermal conductivity and electrical conductivity $(\partial \Pi / \partial T - \alpha) (j, \text{grad } T)$.

The quantity of heat additionally released in a conductor as a consequence of temperature inhomogeneity is called Thomson's heat, and the effect itself is called *Thomson's effect*. Phenomenologically this heat is equal to

$$q_T = \tau (j, \text{grad } T), \quad (11.M)$$

where τ is *Thomson's coefficient*. Proceeding from our analysis we establish that

$$\tau = \frac{\partial \Pi}{\partial T} - \alpha. \quad (11.26)$$

This relation is called *Thomson's first relation*.

Thomson's heat can be positive or negative according to the sign of $(j, \text{grad } T)$. If the direction of either only j or only $\text{grad } T$ reverses,

the quantity q_T changes its sign. For this reason Thomson's effect is sometimes called reversible. We must, however, bear in mind that this "reversibility" has no relation whatsoever to the concept of reversibility that is introduced in connexion with the second law of thermodynamics. In this thermodynamic meaning of reversibility and irreversibility Thomson's phenomenon is irreversible, since it is part of a process that is indissolubly connected with such irreversible processes as thermal conduction and release of heat.

PROBLEM

120. Express Peltier's coefficient Π , Thomson's coefficient τ and the thermoelectromotive force α in terms of the flow of entropy caused by the motion of charged particles.

SOLUTIONS TO PROBLEMS

1. From the second initial proposition of thermodynamics it follows that, when two sub-systems, determined by the parameters a_1 , T_1 and a_2 , T_2 respectively, are in thermal equilibrium, their internal energies will be

$$U_1 = U_1(a_1, T_1), \quad U_2 = U_2(a_2, T_2),$$

and, since $T_1 = T_2$,

$$T_1(a_1, U_1) = T_2(a_2, U_2). \quad (1)$$

The uniqueness of the distribution of the energy of a system among its parts implies that for given a_1 , a_2 , U_2 the equation (1) has only one solution for U_1 . This means that $T_1(a_1, U_1)$ is a monotonic function of U_1 .

From the simultaneous increase of the energy of parts of a system for an increase of its total energy it follows that T_1 , T_2 , T_3 etc. are either simultaneously monotonically increasing, or monotonically decreasing functions of U_1 , U_2 , U_3 etc. respectively. By a simple transformation we can make them monotonically increasing and choose the temperature functions $T = T(a, U)$ so that T will increase for an increase of U . With such a choice of temperature functions the derivative $(\partial U / \partial T)_a$ is positive for all bodies.

2. The state of a system is determined by the temperature T and external parameters a_1, a_2, \dots, a_n . In the expression of the elementary work

$$\delta W = \sum A_i da_i \quad (1)$$

the differential of temperature does not occur (i.e. the coefficient of dT in (1) is equal to zero).

If (1) were the total differential of some function of state of the system, then

$$(\partial A_i / \partial T) = (\partial 0 / \partial a_i) = 0,$$

which would indicate the absence of temperature dependence of the generalized forces (for example, pressure), and this contradicts the initial proposition of thermodynamics on the existence of the equation of state $A = A(a_1, a_2, \dots, a_n; T)$.

3. The elementary work against the forces of pressure is equal to $\delta W = p dV$. For $p = \text{const}$ the work is equal to

$$W = p(V_2 - V_1),$$

where V_1 and V_2 are respectively the volume of a mole of water and the volume of a mole of vapour. Since $V_2 \gg V_1$, then

$$W = pV_2 = p(RT/p) = RT = 2 \cdot 373 \text{ cal} = 318 \cdot 5 \text{ kgm}.$$

The heat of vaporization of a mole of water is equal to

$$Q = \lambda m = 539 \cdot 18 \text{ cal} \approx 4142 \text{ kgm}$$

(λ is the latent heat of vaporization, equal to 539 cal/g for water). The difference $Q - W$, which is considerably larger than W goes into work against the internal forces of cohesion between molecules of liquid in the transformation of liquid into vapour.

4. The dependence of the magnetization M on the magnetic field H in a ferromagnetic substance is represented on the H, M diagram by a hysteresis curve (Fig. 42). The elementary work of magnetization of a unit volume, equal to

$$\delta W = -H dm$$

is represented on this diagram by the shaded area. The work for a double reversal of magnetic polarization of a unit volume of the core of the solenoid is evidently equal to

$$W = -\oint H dm = -S$$

i.e. is equal (with a minus sign) to the area of the loop of the hysteresis curve on the H, M diagram. (If H and M are expressed in units of the CGS system, then the area S on this diagram, and therefore the work, W , will be expressed in ergs.)

5. In thermodynamics, work is assumed to be positive if it is accomplished by a system on external bodies. Therefore the work of external sources for generating an electric field in the dielectric and the work accomplished at the same time by the dielectric have different signs.

Let us determine the elementary work of an isotropic dielectric for a variation, dD , of induction in it. Let us consider a dielectric with permittivity ϵ between the plates, of area S , of a plane capacitor with distance d between them. If on the plates of the capacitor there is found charge of density $\pm \sigma$, then the induction D and the field intensity E in the dielectric are: $D = 4\pi\sigma$, $E = 4\pi\sigma/\epsilon$, while the potential difference between the plates $\varphi_2 - \varphi_1 = Ed = 4\pi\sigma d/\epsilon$. When a charge (de) is carried from one plate to the other the external forces accomplish the work $(\varphi_2 - \varphi_1)de = = Ed \cdot (de)$, and therefore the work of the dielectric is equal to

$$\delta W_1 = -Ed \cdot (de)$$

or

$$\delta W_1 = -Ed \cdot S \cdot d(D/4\pi) = -(V/4\pi) E \cdot dD,$$

since $de = Sd\sigma$ and $Sd = V$ is the volume of the dielectric. Thus the elementary work of polarization per unit volume of an isotropic dielectric will be equal to

$$\delta W = -(1/4\pi) Ed dD,$$

or, since $D = E + 4\pi P$

$$\delta W = -(1/4\pi) Ed dE - Ed dP = -d(E^2/8\pi) - Ed dP.$$

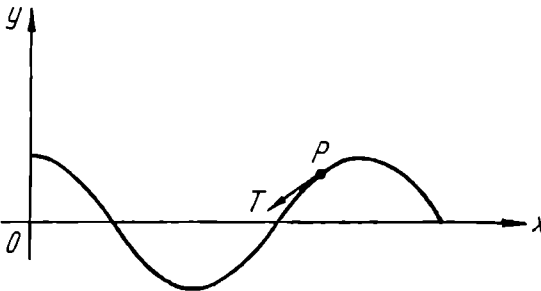


FIG. 43.

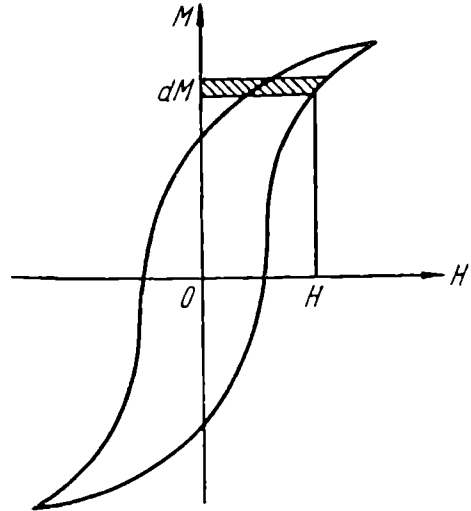


FIG. 42.

The first term in this expression determines the work spent in generating the electric field ($E^2/8\pi$ is the energy density of the electric field in a vacuum); the second term represents the work of polarization proper, per unit volume of an isotropic dielectric

$$\delta W_{\text{proper}} = -Ed dP.$$

6. The equation of a wave propagating along a string with velocity v and frequency ν along the x axis (Fig. 43) has the form

$$y = a \cos \omega (t - xv^{-1})$$

where a is the wave amplitude.

The force that accomplishes work is the tension, T , of the string, which we shall assume to be constant, for small oscillations, both in time and over the length of the string. The left-hand side of the string acts on the right-hand side at the point P with force T along the continuously varying direction of the tangent.

Since the oscillations are transversal, then the displacement of the point P during the time dt is equal to $dy = (\partial y / \partial t) dt$, while the work during this time is equal to

$$\delta W = T dy \cos (T, y) = -T dy \sin (T, x).$$

For small oscillations

$$\sin (T, x) \approx \tan (T, x) = \partial y / \partial x,$$

and therefore

$$\delta W = -T(\partial y / \partial x) dy = -T(\partial y / \partial x)(\partial y / \partial t) dt.$$

The work over a period τ will be

$$W = -T \int_0^{\tau} (\partial y / \partial x)(\partial y / \partial t) dt = Ta^2 \omega^2 v^{-1} \int_0^{2\pi/\omega} \sin^2 \omega(t - xv^{-1}) dt = \pi Ta^2 \omega / v.$$

This work is positive since waves propagate from left to right and in a period the left-hand side of the string transmits to the right-hand side the energy $\pi Ta^2 \omega / v$. For oscillations propagating from right to left, the work will be negative, since in this case $y = a \cos \omega(t + xv^{-1})$ and energy is transmitted from the left-hand to the right-hand side.

7. The second initial proposition of thermodynamics leads to the existence of a thermic equation of state: $A = A(T, a)$ whence

$$dA = (\partial A / \partial a)_T da + (\partial A / \partial T)_a dT.$$

For $dA = 0$ we obtain

$$(\partial A / \partial a)_T \cdot (\partial a / \partial T)_A + (\partial A / \partial T)_a = 0,$$

and

$$(\partial T / \partial A)_a \cdot (\partial A / \partial a)_T \cdot (\partial a / \partial T)_A = -1.$$

In the case of $A = p$ and $a = V$ we have

$$(\partial T / \partial p)_V \cdot (\partial p / \partial V)_T \cdot (\partial V / \partial T)_p = -1.$$

8. By definition, the thermal coefficients are equal to

$$\alpha = V_0^{-1} (\partial V / \partial T)_p, \quad \beta = -V_0^{-1} (\partial V / \partial p)_T, \quad \gamma = p_0^{-1} (\partial p / \partial T)_V,$$

whence

$$\alpha / \beta \gamma = -p_0 (\partial V / \partial T)_p (\partial p / \partial V)_T (\partial T / \partial p)_V.$$

From the identity established in problem no. 7

$$(\partial T / \partial p)_V (\partial p / \partial V)_T (\partial V / \partial T)_p = -1$$

we obtain the following relation between the thermal coefficients

$$\alpha = p_0 \beta \gamma.$$

9. The equation of state of a system cannot be obtained, in thermodynamics, by proceeding merely from the laws of thermodynamics. Therefore in thermodynamic

investigations of the properties of systems these equations are either derived from experiment or are found by the methods of statistical physics. In the case of such a simple system as an ideal gas, the equation of state can also be obtained, without having recourse to general statistical methods, but proceeding from elementary molecular models.

Let us consider an ideal gas of N particles in a cube of side a and volume $V = a^3$. Since under equilibrium conditions the pressure on each face is the same, then on the average on each element of surface of the vessel there will occur the same number of impacts of molecules. We shall satisfy this condition if all molecules in the cube are divided into three groups with $N/3$ molecules in each group, moving perpendicularly to each of the three pairs of opposite faces of the cube. Let the mean velocity with which the molecules move be u . The momentum imparted to the wall for the elastic impact of a molecule is equal to $2mu$ (m is the mass of a molecule). Altogether on each face of area a^2 there are incident in 1 sec $(1/2)(Nu/3V)a^2$ molecules, and therefore the force of pressure on the wall is equal to $2mu \cdot (Nu/6V)a^2 = (Nmu^2/3V)a^2$ and the pressure is $p = Nmu^2/3V$. Hence

$$pV = Nmu^2/3.$$

The intensity of the thermal motion of molecules is characterized in thermodynamics by the temperature T ; by assuming therefore for a mole of gas (when N is Avogadro's number) the kinetic energy of molecules to be proportional to the temperature T , and by taking $Nmu^2/3 = RT$, we obtain Clapeyron's equation for an ideal gas

$$pV = RT.$$

The energy of the entire volume of gas is evidently equal to

$$U = (mu^2/2)N = (3/2)(Nmu^2/3) = (3/2)RT.†$$

This formula is the caloric equation of state of an ideal gas. It can be seen from it that the energy of an ideal gas depends on temperature only but does not depend on volume.

10. Van der Waals' equation $(p + aV^{-2})(V - b) = RT$ can be written in the form

$$V^3 - (RTp^{-1} + b)V^2 + ap^{-1}V - abp^{-1} = 0.$$

It can be seen from this that at a given temperature T to one value of p there correspond three values of V , so that on the V, p diagram (Fig. 44) a straight line parallel to the axis of the abscissae (an isobaric) intersects an isothermal, in general, at three points. At high temperatures two roots are imaginary and to each value of pressure there always corresponds only one value of volume. At lower temperatures for a given value of pressure three real values of volume are possible. Of these three values, denoted on the diagrams as the points α , β and γ , only the extreme ones α and γ can be obtained in nature; the state β is impossible since it is absolutely unstable, owing to the fact that, for a stable state at constant temperature, pressure decreases with an increase of volume (see § 31). The point α corresponds to liquid, and the point γ to the gaseous state of the given substance. Of these two states, however, only one, corresponding to the point α , is stable. As experiment shows, in compressing a gas, a determined point C on the isothermal is reached and, by further isothermal compression, the representative point does not move beyond C along the theoretical curve; the gas is liquefied and the gaseous, C , and liquid, A , states exist at the same

† The mean energy of thermal motion of a molecule at the temperature T is equal to $mu^2/2 = (3/2)(R/N)T = (3/2)kT$, where $k = R/N = 8.3144 \times 10^7/6.0235 \times 10^{23} = 1.38 \times 10^{-16}$ erg/degree (Boltzmann's constant).

time in equilibrium, having the same temperature and pressure. The simultaneous existence of these two states continues for isothermal compression until all the gas passes to liquid. Therefore of the states α and γ only the state α will be stable, and the state γ metastable.

The question of where to draw on the theoretical curve the straight line CBA corresponding to the real behaviour of pressure can be answered by using Maxwell's rule (which is easily established on the basis of the second law of thermodynamics (see problem no. 48)): the areas bounded by the van der Waals' curve and the straight line CBA above and below this line must be equal.

As temperature increases the difference between the volumes V_c and V_A decreases, the straight segment ABC becomes smaller and smaller and at a certain temperature the points A , B and C merge with one another, so that the corresponding isobaric intersects such an isothermal at a single point. This point is therefore an inflection point of the isothermal, the tangent to which is parallel to the axis of the abscissae. It determines the critical state of a substance, called the *critical point* and is characterized by a determined critical temperature T_{cr} , critical volume V_{cr} and critical pressure p_{cr} . In this state the system represents, from the macroscopical viewpoint, a single phase. (For more details on the critical state see Chapter VIII).

Since the coordinates of the critical point satisfy the van der Waals' equation $(p + a/V^2)(V - b) = RT$ and the equations $(\partial p / \partial V)_T = 0$, $(\partial^2 p / \partial V^2)_T = 0$, then the

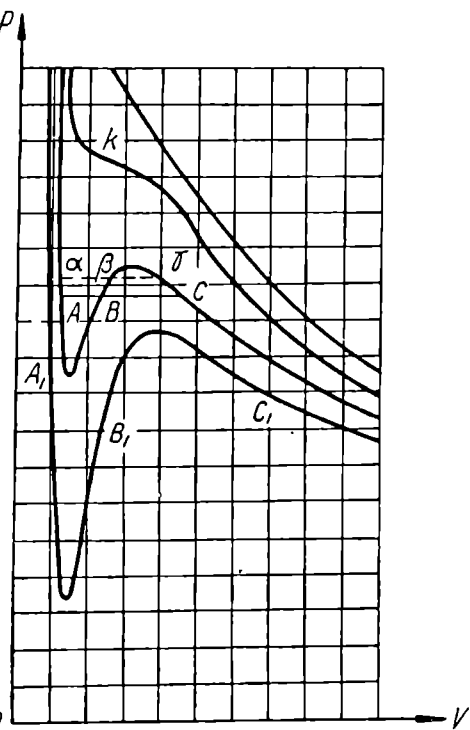


FIG. 44.

critical parameters p_{cr} , V_{cr} , T_{cr} are determined by the simultaneous solution of these equations. We shall then obtain

$$V_{cr} = 3b, \quad p_{cr} = a/27b^2, \quad T_{cr} = 8a/27Rb.$$

These parameters can also be found by proceeding from the fact that van der Waals' equation has at the critical state three equal roots and must therefore have the form $(V_{cr} - V)^3 = 0$ or $V^3 - 3V_{cr}V^2 + 3V_{cr}^2V - V_{cr}^3 = 0$. By comparing this equation with van der Waals' equation at the critical point

$$V^3 - (RT_{cr}p_{cr}^{-1} + b)V^2 + ap_{cr}^{-1}V - abp_{cr}^{-1} = 0,$$

we obtain

$$3V_{cr} = RT_{cr}p_{cr}^{-1} + b, \quad 3V_{cr}^2 = ap_{cr}^{-1}, \quad V_{cr}^3 = abp_{cr}^{-1},$$

whence, by dividing the third of these equations by the second, we shall obtain $V_{cr} = 3b$, which, together with the third equation gives $p_{cr} = a/27b^2$, while from the first equation we find $T_{cr} = 8a/27Rb$.

The critical coefficient $s = RT_{cr}/p_{cr}V_{cr}$ for van der Waals' equation is thus equal to $s = 8/3 = 2.67$, i.e. it has one and the same value for all substances (it does not depend on a and b). In actual fact s has different values for different gases; it is always larger than 2.67 and has on the average the value $s \approx 3.7$.

11. For a gas the state of which is determined by Dieterici's first equation

$$p(V - b) = RT \exp(-a/RTV), \quad (1)$$

the critical parameters p_{cr} , V_{cr} and T_{cr} can be found by solving this equation simultaneously with the equations $(\partial p/\partial V)_T = 0$, $(\partial^2 p/\partial V^2)_T = 0$. By differentiating (1) with respect to V for constant T once and twice, and equating these derivatives to zero, we shall obtain together with (1) the system of equations

$$\begin{aligned} p_{cr}(V_{cr} - b) &= RT_{cr} \exp(-a/RT_{cr}V_{cr}), \\ p_{cr} &= aV_{cr}^{-2} \exp(-a/RT_{cr}V_{cr}), \\ 0 &= aR^{-1}T_{cr}^{-1}V_{cr}^{-1} - 2, \end{aligned}$$

whence

$$p_{cr} = a/4e^2b^2, \quad V_{cr} = 2b \quad T_{cr} = a/4Rb.$$

The critical coefficient s is equal to

$$s = \frac{RT_{cr}}{p_{cr}V_{cr}} = e^2/2 = 3.695,$$

which agrees well with experimental data for many substances, for which s varies within the range 3.5 to 3.95. The critical coefficient obtained for van der Waals' equation is equal to 2.67 (see problem no. 10).

For large volumes V , Dieterici's equation reduces to van der Waals' equation. In fact by expanding $\exp(-a/RTV)$ with respect to the quantity a/RTV , which is small for large values of V , and stopping at the second term of the expansion we shall from Dieterici's equation obtain the equation

$$p(V - b) = RT(1 - aR^{-1}T^{-1}V^{-1}),$$

or

$$p(V - b) = RT - aV^{-1}.$$

For large values of V the quantities a/V and b/V are small, and therefore

$$V^{-1}a \approx V^{-1}a(1 - bV^{-1}),$$

we obtain

$$(p + aV^{-2})(V - b) = RT.$$

12. The critical parameters p_{cr} , V_{cr} and T_{cr} for a substance the equation of state of which is Dieterici's second equation

$$(p + aV^{-1/2})(V - b) = RT$$

are found by solving this equation simultaneously with the equations $(\partial p/\partial V)_T = 0$ and $(\partial^2 p/\partial V^2)_T = 0$. We shall then obtain

$$p_{cr} = a/4(4b)^{1/2}, \quad V_{cr} = 4b, \quad T_{cr} = 5ab/4R(4b)^{1/2}.$$

The critical coefficient s is equal to

$$s = RT_{cr}/p_{cr}V_{cr} = 3.75,$$

which agrees well with experimental data for so-called "normal substances", for which s varies within the range 3.5 to 3.95. In this respect Dieterici's second equation gives a better result than van der Waals' equation, which leads to a value of the critical coefficient $s = 2.67$ (see problem no. 10).

13. By replacing in van der Waals' equation

$$(p + aV^{-2})(V - b) = RT$$

p , V and T by πp_{cr} , φV_{cr} and τT_{cr} respectively, and replacing a , b and R by their ex-

pressions in terms of p_{cr} , V_{cr} and T_{cr} (see problem no. 10), we shall obtain van der Waals' reduced equation

$$(\pi + 3\varphi^{-2})(3\varphi - 1) = 8\tau$$

which contains no constants depending on the nature of the substance. This equation expresses the law of the corresponding states: if two of the reduced variables π , φ and τ coincide for different substances, then the third variable also coincides and the states of these substances will be *corresponding*.

Similarly, by replacing in Dieterici's first equation

$$p(V-b) = RT \exp(-a/RTV)$$

p , V and T by πp_{cr} , φV_{cr} and τT_{cr} respectively and replacing a , b and R by their expressions in terms of the critical parameters p_{cr} , V_{cr} and T_{cr} (see problem no. 11), we shall obtain Dieterici's first reduced equation

$$\pi(2\varphi - 1) = \tau \exp[2(1 - \tau^{-1}\varphi^{-1})].$$

A reduced equation can be obtained for every equation of state in which there are not more than three constants depending on the nature of the substance. This follows from the fact that in determining the critical parameters p_{cr} , V_{cr} and T_{cr} from the three equations

$$p = p(V, T), \quad (\partial p / \partial V)_T = 0 \text{ and } (\partial^2 p / \partial V^2)_T = 0$$

we obtain for them values that are expressed in terms of the constants occurring in the equation of state, and if these constants depending on the nature of the substance are more than three in number, then it is evidently impossible to express them in terms of only p_{cr} , V_{cr} and T_{cr} .

A reduced equation enables us to indicate more accurately criteria for which the equation of state of an ideal gas can be a good approximation to reality. We shall show, for example, that in all cases when the volume of gas is large in comparison with its critical volume, van der Waals' equation reduces to Clapeyron's equation, and therefore the approximation of an ideal gas agrees well in such cases with reality.

Van der Waals' reduced equation

$$(\pi + 3\varphi^{-2})(3\varphi - 1) = 8\tau$$

can be written approximately, in the case when $\varphi = V/V_c \gg 1$, in the form $\pi\varphi = (8/3)\tau$. Since, however, the critical coefficient $s = RT_{cr}/p_{cr}V_{cr}$ for a van der Waals' gas is equal to $8/3$, this equation will be written thus

$$\pi\varphi = (RT_{cr}/p_{cr}V_{cr})\tau$$

or

$$(p/p_{cr})(V/V_{cr}) = (RT_{cr}/p_{cr}V_{cr})(T/T_{cr})$$

and therefore

$$pV = RT.$$

14. If the equation of state is written in the standard form (1.25):

$$pV = RT(1 + AV^{-1} + BV^{-2} + CV^{-3} + \dots),$$

then the quantities A , B , C etc. are called, as we know (see page 35), the first, second, third etc. virial coefficients respectively. It is evident that for an ideal gas all virial coefficients are equal to zero. By representing van der Waals' equation in its standard form, we can find the virial coefficients of a van der Waals' gas. From

$$(p + aV^{-2})(V - b) = RT$$

we obtain

$$p = RT(V - b)^{-1} - aV^{-2}$$

and

$$pV = RT(1 - bV^{-1})^{-1} - aV^{-1}.$$

Since $b/V \ll 1$, then

$$RT(1 - bV^{-1})^{-1} = RT(1 + bV^{-1} + b^2V^{-2} + b^3V^{-3} + \dots)$$

and therefore

$$pV = RT[1 + (b - aR^{-1}T^{-1})V^{-1} + b^2V^{-2} + b^3V^{-3} + \dots],$$

whence the first and second virial coefficients of a van der Waals' gas are

$$A = b - aR^{-1}T^{-1}, \quad B = b^2.$$

From the condition $A = b - aR^{-1}T^{-1} = 0$ we find Boyle's temperature $T_B = a/Rb$. The equation of an ideal gas (Boyle-Mariotte equation) is applicable at this temperature for a given real gas.

Boyle's point has an important role in the liquefaction of gases. As is found (see § 24), a van der Waals' gas at a temperature higher than $2T_B$ cannot be cooled by irreversible expansion (Joule-Thomson effect).

15. Since the elementary work δW occurring in the equation $\delta Q = dU + \delta W$ is not an exact differential (see problem no. 2) then also δQ is not the total differential of any function of the independent variables. We can verify this also directly.

According to the first law of thermodynamics for a simple system

$$\delta Q = (\partial U / \partial T)_V dT + [(\partial U / \partial V)_T + p] dV.$$

If δQ were an exact differential, then the reciprocity condition would be satisfied

$$\left\{ \partial(\partial U / \partial T)_V / \partial V \right\}_T = \left\{ \partial[(\partial U / \partial V)_T + p] / \partial T \right\}_V,$$

or

$$(\partial p / \partial T)_V = 0$$

which contradicts the general proposition of the existence of an equation of state and, in particular, experiments on the temperature dependence of the pressure of a system.

16. The equation of the first law of the thermodynamics for a simple system in terms of the independent variables T and p has the form

$$\begin{aligned} \delta Q &= dU + p dV = d(U + pV) - V dp = dH - V dp \\ &= (\partial H / \partial T)_p dT + [(\partial H / \partial p)_T - V] dp. \end{aligned}$$

Hence

$$\delta Q / dT = (\partial H / \partial T)_p + [(\partial H / \partial p)_T - V] dp / dT$$

and

$$\begin{aligned} C_p &= (\partial H / \partial T)_p, \\ C_V &= (\partial H / \partial T)_p + [(\partial H / \partial p)_T - V] (\partial p / \partial T)_V, \\ C_p - C_V &= [V - (\partial H / \partial p)_T] (\partial p / \partial T)_V. \end{aligned}$$

17. The velocity of propagation, u , of longitudinal waves in an elastic medium is equal to

$$u = (\varepsilon / \rho)^{1/2},$$

where ε is the elasticity modulus and ρ is the density of the medium. The rapidity of compression and rarefaction of an elastic medium propagating sound is so large that no heat exchange occurs in the time of a period, and therefore the process of sound propagation is adiabatic. Hence

$$u = (\varepsilon_S / \rho)^{1/2} = (\gamma \varepsilon_T / \rho)^{1/2} = V[-\gamma \mu^{-1} (\partial p / \partial V)_T]^{1/2},$$

since

$$\varepsilon_S/\varepsilon_T = \gamma, \quad \varepsilon_S = -V(\partial p/\partial V)_S, \quad \varepsilon_T = -V(\partial p/\partial V)_T,$$

and $\varrho V = \mu$ is the molecular weight of the gas.

The derivative $(\partial p/\partial V)_T$ can be found if the thermic equation of state of the gas is known. In the case of an ideal gas

$$pV = RT, \quad (\partial p/\partial V)_T = -RT/V^2$$

and

$$u = (\gamma RT/\mu)^{1/2}.$$

18. According to (2.7)

$$C_A - C_a = [(\partial U/\partial a)_T + A](\partial a/\partial T)_A.$$

For a paramagnetic substance $A = -H$, $a = M$ and therefore

$$C_H - C_M = [(\partial U/\partial M)_T - H](\partial M/\partial T)_H.$$

In the case of an ideal paramagnetic substance, when $(\partial U/\partial M)_T = 0$, by using the thermic equation of state $M = \kappa H$, where the permeability according to Curie's law is equal to $\kappa = C/T$ (C is Curie's constant), we obtain

$$C_H - C_M = CH^2/T^2.$$

19. From the general equation of an adiabatic (2.19)

$$(\partial T/\partial A)_a dA + \gamma(\partial T/\partial a)_A da = 0$$

in the case of a paramagnetic substance, when $A = -H$ and $a = M$, we have

$$(\partial T/\partial H)_M dH + \gamma(\partial T/\partial M)_H dM = 0.$$

Since for an ideal paramagnetic substance

$$M = \kappa H = CH/T$$

(C is Curie's constant) and

$$(\partial T/\partial H)_M = C/M, \quad (\partial T/\partial M)_H = -CH/M^2,$$

then the differential equation of an adiabatic for an ideal paramagnetic substance will be

$$dH/H = \gamma dM/M,$$

whence, by taking into account that $\gamma = C_H/C_M = \text{const}$, we obtain, after integration, the equation

$$HM^{-\gamma} = \text{const}.$$

20. The gas expands polytropically and therefore $p_1 V_1^n = p_2 V_2^n$ or $4V^n = (3V)^n$ whence the index of the polytropic is equal to

$$n = \log 4/\log 3 = 1.26$$

The work in the polytropic process is

$$W = \int_{V_1}^{V_2} p dV = \int_{V_1}^{V_2} \text{const } V^{-n} dV = \text{const } (1-n)^{-1} [V^{1-n}]_{V_1}^{V_2} =$$

$$(p_2 V_2 - p_1 V_1)/(1-n) = 0.26^{-1}(4[5 \times 10^4] - 15 \times 10^4) = 192,300 \text{ kgm}.$$

The heat transferred in the polytropic process is

$$Q = mc(t_2 - t_1),$$

where m is the mass of gas, c is the polytropic specific thermal capacity, which can be expressed in terms of the index of the polytropic and other quantities. As is known,

$$n = (c_p - c)/(c_V - c),$$

whence

$$c = c_V(n - \gamma)/(n - 1).$$

Thus

$$Q = mc_V(t_2 - t_1)(n - \gamma)/(n - 1).$$

However, $mc_V(t_2 - t_1) = \Delta U$ is the variation of internal energy of the gas which, by the first law, is equal to $\Delta U = Q - W$, and therefore

$$Q = (Q - W)(n - \gamma)/(n - 1),$$

whence ($\gamma = 1.4$)

$$Q = W(\gamma - n)/(\gamma - 1) = 157.4 \text{ kcal}$$

and

$$\Delta U = Q - W = -293 \text{ kcal}.$$

The expansion work is accomplished by the gas at the expense of the heat communicated to it and the decrease of its internal energy.

21. The elasticity modulus ϵ and the elasticity coefficient k are quantities reciprocal to each other

$$\epsilon = 1/k.$$

In the general case of a simple system when the generalized force is A and the external parameter associated with it is a , the ratio of the adiabatic and isothermal moduli is equal to

$$\epsilon_S/\epsilon_T = C_A/C_a$$

and therefore

$$k_T/k_S = C_A/C_a.$$

In the case investigated: $A = p$, $a = l$, and therefore the ratio of the coefficients of isothermal and adiabatic linear expansion, λ_T and λ_S is equal to

$$\lambda_T/\lambda_S = C_p/C_l.$$

where C_p and C_l are respectively the thermal capacity of the rod for a constant tension force p and for a constant length l .

22. The permeability ($\partial M/\partial H$) in adiabatic and isothermal processes corresponds not to the modulus but to the elasticity coefficient for these processes, and therefore according to the general formula for the ratio of these coefficients (see problem no. 21) we obtain

$$k_T/k_S = C_A/C_a.$$

In the case given $A = -H$ and $a = M$ and therefore

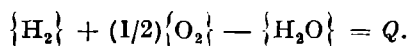
$$k_T/k_S = C_H/C_M$$

and

$$(\partial M/\partial H)_T/(\partial M/\partial H)_S = C_H/C_M,$$

where C_H and C_M are the thermal capacities of the magnetic substance for a constant magnetic field H and constant magnetization M respectively.

23. We have to determine the heat of formation of water vapour from its elements i.e. Q from the thermochemical equation



The thermochemical equations of formation and vaporization of water will be

$$\begin{aligned}\{\text{H}_2\} + (1/2)\{\text{O}_2\} - (\text{H}_2\text{O}) &= Q_1 \\ (\text{H}_2\text{O}) - \{\text{H}_2\text{O}\} &= -Q_2.\end{aligned}$$

By adding these equations we shall obtain

$$\{\text{H}_2\} + (1/2)\{\text{O}_2\} - \{\text{H}_2\text{O}\} = Q_1 - Q_2.$$

Hence the heat of formation of water vapour from its elements is equal to

$$Q = Q_1 - Q_2 = 68.4 - 9.5 = 58.9 \text{ kcal/mole},$$

which is greater than zero; therefore heat is evolved in the formation of water vapour from its elements.

24. The heat Q of formation of methane from solid carbon and gaseous hydrogen is determined by the thermochemical equation

$$[\text{C}] + 2\{\text{H}_2\} - \{\text{CH}_4\} = Q.$$

The thermochemical equations of the complete combustion of methane in carbon dioxide and water, of the formation of water from its elements, and of the complete combustion of carbon will be respectively

$$\begin{aligned}\{\text{CH}_4\} + 2\{\text{O}_2\} - \{\text{CO}_2\} - 2(\text{H}_2\text{O}) &= Q_1, \\ \{\text{H}_2\} + (1/2)\{\text{O}_2\} - (\text{H}_2\text{O}) &= Q_2, \\ [\text{C}] + \{\text{O}_2\} - \{\text{CO}_2\} &= Q_3.\end{aligned}$$

By multiplying the second equation by two, adding it after this to the third equation, and subtracting the first equation from the result, we shall obtain

$$[\text{C}] + 2\{\text{H}_2\} - \{\text{CH}_4\} = 2Q_2 + Q_3 - Q_1.$$

Thus the heat of formation of methane from solid carbon and gaseous hydrogen is equal to

$$Q = 2Q_2 + Q_3 - Q_1 = 21.9 \text{ kcal/mole}.$$

25. The dependence of the heat of reaction on temperature is determined by Kirchhoff's equation which is easily established by differentiating with respect to temperature the expression for Q given by the first law of thermodynamics.

If a reaction occurs for $V = \text{const}$, then, according to the first law of thermodynamics

$$Q = U_2 - U_1,$$

and the heat effect of the reaction $\bar{Q} = -Q = U_1 - U_2$. By differentiating this expression with respect to T , we shall obtain Kirchhoff's equation for the temperature dependence for the heat of reaction in isochoric processes

$$(\partial\bar{Q}/\partial T)_V = (\partial U_1/\partial T)_V - (\partial U_2/\partial T)_V = (C_V)_1 - (C_V)_2.$$

In isobaric transformations

$$Q = (U_2 + pV_2) - (U_1 + pV_1) = H_2 - H_1,$$

and

$$\bar{Q} = H_1 - H_2,$$

where $H = U + pV$.

The derivative of H with respect to T for $p = \text{const}$ is equal to C_p ; in fact

$$\begin{aligned}\delta Q &= dU + p dV = d(U + pV) - V dp = dH - V dp \\ &= (\partial H / \partial T)_p dT + [(\partial H / \partial p)_T - V] dp,\end{aligned}$$

whence

$$C_p = (\partial Q / \partial T)_p = (\partial H / \partial T)_p.$$

Thus Kirchhoff's equation for the temperature dependence of the heat of reaction in isobaric processes will be

$$(\partial \bar{Q} / \partial T)_p = (\partial H_1 / \partial T)_p - (\partial H_2 / \partial T)_p = (C_p)_1 - (C_p)_2.$$

The subscripts 1 and 2 here denote the corresponding thermal capacities of the system before the reaction and after the reaction.

In order to find the variation, with temperature, of the heat of combustion of a mole of hydrogen into (liquid) water we shall subtract from the thermal capacity $(C_p)_1$ of a mixture consisting of a mole of hydrogen and half a mole of oxygen, the thermal capacity of a mole of water $(C_p)_2$.

The molecular thermal capacity of diatomic gases (hydrogen, oxygen) at constant volume is equal to $5 \text{ cal/mole} \times \text{degree}$, while $C_p = C_V + R = 7 \text{ cal/mole} \times \text{degree}$. Therefore $(C_p)_1 = 7 + (7/2) = 10.5 \text{ cal/mole} \times \text{degree}$; $(C_p)_2 = 18 \text{ cal/mole} \times \text{degree}$ and therefore $(\partial \bar{Q} / \partial T)_p = 10.5 - 18 = -7.5 \text{ cal/mole} \times \text{degree}$, i.e. for an increase of temperature by 1°C the heat evolved in the combustion of a mole of hydrogen into liquid water decreases by 7.5 cal .

26. Let a process be represented by the polytropic AD' (Fig. 45). Let us draw through D' the adiabat S_1 and the isothermal T_1 . The isothermal T lies on the p, V diagram above the isothermal T_1 and therefore, as follows from $pV = RT$, its temperature is correspondingly higher. From the equation of the adiabat $pV^\gamma = \text{const} = C$ ($\gamma = C_p/C_V > 1$) it follows that the higher adiabat has a correspondingly larger value of C . In addition, according to the first law we have for an ideal gas

$$\delta Q = C_V dT + p dV$$

and, since from $pV = RT$

$$dT = (pdV + Vdp)/R,$$

then

$$\begin{aligned}R\delta Q &= C_V V dp + C_p p dV = C_V p V (p^{-1} dp + \gamma V^{-1} dV) \\ &= C_V p V d[\log_e(pV^\gamma)] = C_V p V d(\log_e C),\end{aligned}$$

whence it can be seen that the passage to a higher adiabat (when C increases) is accompanied by absorption of heat.

Thus in the polytropic process AD' when we pass from the lower to the higher adiabat and from the higher to the lower isothermal $\delta Q > 0$ while $dT < 0$ and therefore the thermal capacity $C = \delta Q/dT$ in such a process is negative. In the process $D'A$ or AD the thermal capacity is also negative since now $\delta Q < 0$ while $dT > 0$. In processes with negative thermal capacity the work accomplished by the system

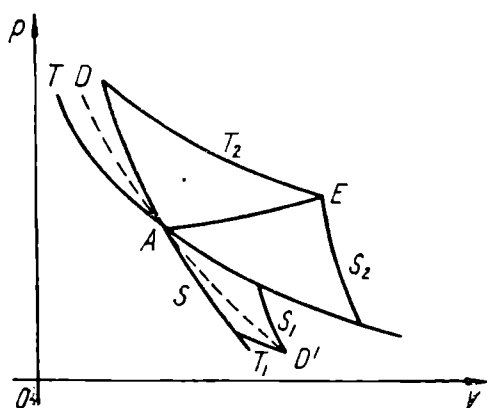


FIG. 45.

is larger than the quantity of heat obtained by it ($\delta Q > 0$, $dT < 0$) or, vice versa, the work done on the system is larger than the heat released ($\delta Q < 0$, $dT > 0$).†

In the process AE there occurs absorption of heat and increase of temperature, since $T_2 > T$ and $S_2 > S$, and therefore this process occurs with a positive thermal capacity.

27. From $\delta Q = C_a dT + [(\partial U/\partial a)_T + A] da$ it can be seen that in an adiabatic process ($\delta Q = 0$)

$$C_a dT_S + [(\partial U/\partial a)_T + A] da = 0.$$

This process will also be, at the same time, isothermal ($dT_S = 0$), if the following condition is satisfied for arbitrary values (positive or negative) of da

$$[(\partial U/\partial a)_T + A]/C_a = 0. \quad (1)$$

When this condition is not satisfied, temperature always varies in an adiabatic process ($dT_S \neq 0$), while the heat exchange in an isothermal process ($dT = 0$) is not equal to zero:

$$\delta Q_T = [(\partial U/\partial a)_T + A] da \neq 0,$$

and therefore the adiabatic does not coincide with the isothermal.

From the fact that adiabatic and isothermal do not coincide it does not follow at all (as is sometimes stated)‡ that an arbitrary state of equilibrium of the system, that can be reached from a given state by means of an isothermal process ($dT = 0$), cannot be reached by an adiabatic process ($\delta Q = 0$) or, in other words, that in the vicinity of each equilibrium state such states exist that cannot be reached from it adiabatically (the principle of adiabatic unattainability).

In fact, one and the same variation dU for the passage of a system from one state to another can be achieved with $\delta Q - \delta W = \text{const}$, which can be, according to the first law, both for $\delta Q = 0$ and for $\delta Q \neq 0$. The result of adiabatic unattainability for the case when the condition (1) is not satisfied, i.e. when an adiabatic does not coincide with an isothermal, can be derived only on the basis of the second law of thermodynamics (see § 13). Vice versa, in the opposite case when a system is found in such a state for which the condition (1) is satisfied, i.e. when an adiabatic process in the system coincides with an isothermal process $T_1 = \text{const}$, the result of adiabatic unattainability follows automatically from the definition of temperature, since we cannot make a system pass isothermally (and therefore, in the case given, also adiabatically) from a state with temperature T_1 to a neighbouring state with temperature $T_1 + dT$; and therefore in the vicinity of each state there exist such states that are unattainable by adiabatic means. From this there also follows the adiabatic unattainability of the states themselves that have temperature T_1 (see problem no. 46). Such states are, however, attainable by other, non-adiabatic, means.

If, on the other hand, at a certain temperature T_0 , not only is the condition (1) satisfied but, in addition, the thermal capacity is equal to zero, then non-adiabatic processes become impossible, and therefore states with temperature T_0 are absolutely unattainable. In fact, when the condition (1) is satisfied, $\delta Q = C_a dT$ and therefore for $\delta Q = 0$ dT will also be equal to zero (the adiabatic coincides with the isothermal); if then, in addition, also $C_a = 0$, then δQ is always equal to zero, i.e. the system will behave in all cases as an adiabatically isolated system, and therefore states with temperature T_0 are unattainable. This result can be called the principle of unattainability.

† As an example of the latter type of process we can cite processes in stars, where gravitational forces accomplish, in compression, more work than the heat irradiated.

‡ See N. I. Belokon, *Thermodynamics* (Termodinamika), Gosenergoizdat, page 145 (1954).

bility of the temperature T_0 . By means of (1) and using the second law we can establish a connexion between certain parameters of state of a system for which states with $T_0 = 0^\circ\text{K}$ are unattainable. This connexion, however, does not follow directly from the first and second laws of thermodynamics, and therefore the result of the unattainability of the absolute zero temperature cannot be obtained from these laws—new experimental data are needed. Such data were obtained by Nernst's investigations (see Chapter IX).

28. Such a process is possible, but according to the second law of thermodynamics it is also connected with compensation. Compensation in the conversion of heat into work can consist not only in the transmission of a portion of heat to the cooler, but also in a variation of the state of the working body if the process is not of the closed-cycle type. For example, in the case of an ideal gas for which the internal energy does not depend on volume, the heat taken from the heater in an isothermal process is entirely converted into expansion work; the compensation in such a process will be the variation of volume of the gas. If we eliminate this variation by contracting the gas to its previous volume, the work previously obtained must now be expended on ceding the heat taken from the heater.

29. The error in Wien's reasoning consists in the following. The light from the second body that returns to it after reflection from prism I undergoes, in passing through the rotating layer, one more rotation by 45° and therefore will not be transmitted by prism II and, having undergone in it complete internal reflection, will return (if one more mirror is placed against S_2) to the first body. Thus the second law of thermodynamics is not infringed and there is no need to invoke any unknown phenomena causing compensation.

The Wien paradox expounded here is discussed in volume V of the complete works of Academician L. I. Mandel'shtam.

30. The experiment described not only does not contradict the second law, but has been specially devised by Darlington for a transparent illustration of this law.

The motion of the aniline drop is caused by the fact that, on heating the glass, aniline becomes lighter than water as a consequence of its larger coefficient of thermal expansion and comes to the water surface in the form of a drop; here, coming into contact with air, aniline is cooled, becomes again heavier than water and sinks to the bottom of the vessel. Then the whole process is repeated anew. In this experiment we have an original heat engine in which the heater is the sand bath and the cooler is atmospheric air.

31. As water evaporates from the wet head of the duckling its temperature is somewhat lowered; as a consequence of this the vapour tension in the head part becomes smaller than the vapour tension in the sector A (see Fig. 11), liquid rises to the head and the head drops. As the stem bends forwards its end rises above the liquid surface and the pressure in A and at the stem are equalized. Liquid flows down away from the head, and the head rises. The cyclical process will continue as long as the head remains wet. In this "engine" the heater is the surrounding medium, and cooling is caused by evaporation of the water. If the duckling and the little glass containing water are covered with a bell, after a certain time the air under the bell will become saturated with water vapour and, as no temperature difference can now arise from evaporation, the oscillations of the duckling will cease. After removal of the bell the duckling will start again oscillating by itself. At low temperature or in the presence of high humidity in air (for example, after rain) the duckling slows down markedly its motion and can stop.

32. The process of mixing and separation of gases can be accomplished reversibly by means of selectively permeable diaphragms. Two types of devices are possible here. In one type the mixed gases have the facility to expand reversibly and to accomplish work, while in the other type gases have no such facility and separation is carried out without accomplishing work.

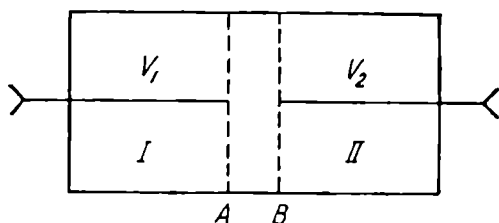


FIG. 46.

A set-up corresponding to the first case is shown in Fig. 46; the gas *I* is separated from the gas *II* in the cylinder by means of two selectively-permeable pistons: *A* is permeable for the gas *I* but impermeable for the gas *II*, and *B* is permeable for *II* and impermeable for *I*. The piston *A* will move under the pressure of the gas *II* and the piston *B* under the pressure of the gas *I*. If these gas pressures on the

pistons are equilibrated by external pressures on the pistons and the whole apparatus is immersed in a large bath whose temperature is T , mixing can be carried out isothermally and reversibly. By exerting pressure on the pistons, a mixture of gases can be irreversibly separated into its component parts.

The work accomplished in the expansion of the gases is evidently equal to

$$W = \int_{V_1}^{V_1+V_2} p dV = v_1 RT \log_e [(V_1 + V_2)V_1^{-1}] + v_2 RT \log_e [(V_1 + V_2)V_2^{-1}]$$

where v_1 and v_2 are the numbers of moles of the gases *I* and *II* respectively. For $v_1 = v_2 = 1$ and therefore $V_1 = V_2$ the work $W = 2RT \log_e 2$.

In a set-up corresponding to the second case (Fig. 47) the mixture of two gases occupies the volume V formed by two cylinders fitting in one another. The cylinders have semipermeable walls and are insulated from the surrounding medium. The left-hand wall *A* of the right-hand vessel is permeable only for the first gas, and the right-hand wall of the left-hand vessel is permeable only for the second gas. When the vessels are pushed together, their volume is occupied by a mixture of the two gases. As the vessels are pulled apart, the pressure in the part *I* will be p_1 , in the part (*I* + *II*) the pressure will be $p_1 + p_2$, and in the part *II* the pressure is equal to p_2 . On the left and on the right of the wall of the left-hand vessel the pressure is equal to p_1 . Therefore on the whole left-hand vessel there acts a force equal to zero and therefore the work for a displacement of the vessel is also equal to zero. Separation of the mixture in the case considered occurs without expenditure of work or admission of heat. The mixing of gases carried out in a similar manner will also be reversible.

If in the second set-up the gases are not different but identical then, by displacing the first vessel the mixture will not be separated but will expand and therefore the gas will accomplish work and will cool; in the presence of a thermostat the temperature of the mixture will be constant and heat will be abstracted from it.

33. (a) The temperature of the mixture is $T = (T_1 + T_2)/2$;

$$\Delta S = \int_{T_1}^T T^{-1} \delta Q + \int_{T_2}^T T^{-1} \delta Q; \quad \delta Q = mcdT,$$

and therefore

$$\Delta S = mc \log_e (T/T_1) + mc \log_e (T/T_2) = mc \log_e [(T_1 + T_2)^2 / 4T_1T_2] > 0$$

since

$$(T_1 + T_2)^2 > 4T_1T_2.$$

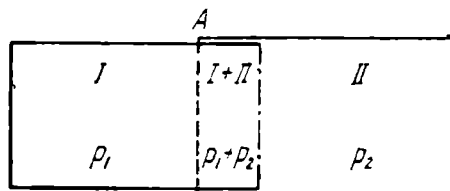


FIG. 47.

(b) The gas pressure after mixing is $p = (p_1 + p_2)/2$, since the internal energies of the gases before and after mixing are equal to: $p_1 V/(\gamma - 1)$, $p_2 V/(\gamma - 1)$ and $2pV/(\gamma - 1)$. Therefore

$$\Delta S = m[c_V \log_e (p/p_1) + c_V \log_e (p/p_2)] = mc_V \log_e [(p_1 + p_2)^2/4p_1 p_2] > 0.$$

34. In the case of a thermally inhomogeneous equilibrium system the principle of adiabatic irreversibility, and therefore also holonomicity, may not be verified. Let us show this by means of a simple example given by T. A. Afanas'yeva-Ehrenfest.

Let us consider in a closed envelope two ideal gases having different thermal capacities C_1 and C_2 , each taken in the quantity of one mole and separated from each other by a piston which does not transmit heat. We have for each system

$$\begin{aligned} \delta Q &= \delta Q_1 + \delta Q_2 = C_1 dT_1 + p dV_1 + C_2 dT_2 + p dV_2 = \\ &= (C_1 + R) dT_1 + (C_2 + R) dT_2 - (R/p) (T_1 + T_2) dp, \end{aligned} \quad (1)$$

where p is the common pressure of the system.

The independent parameters are T_1 , T_2 and p . It can easily be verified that the condition (3.12) is not satisfied for (1), and therefore the form (1) is non-holonomic. The left-hand side of (3.12) is found here to be equal to $(C_1 - C_2)R/p$ and reduces to zero only for $C_1 = C_2$. This result for a thermally inhomogeneous system means that the entropy of such a system requires a special definition. By entropy of a thermally inhomogeneous system is usually meant the sum of the entropies of its thermally homogeneous parts.

35. The error in Planck's proof consists in the following. As long as we do not know anything about our system S , we cannot rule out that a closed-cycle process may close for it before the ideal gas reaches the same adiabetic from which it has started. Therefore, if we restrict ourselves to take care of the fact that the system shall accomplish a closed-cycle process in combination with the gas we could also obtain the following equation:

$$\oint_S T^{-1} \delta Q + \int_G T^{-1} \delta Q = 0,$$

where $\oint_S T^{-1} \delta Q$ would now denote an integral not taken along a closed path, i.e. $\oint_G T^{-1} \delta Q$ could also be different from zero and therefore $\delta Q/T$ for the system S could also not be an exact differential.

36. (a) Since the entropy remains constant along an adiabetic, then the intersecting of adiabatics would signify the non-uniqueness of entropy, in contradiction to the second law which states its uniqueness.

(b) Let us suppose that the isothermal $TABC$ (Fig. 48) intersects twice the adiabetic $SADC$ (at the points A and C).

Then, as can be seen from the figure, work along the closed-cycle process $ABCD$ is not equal to zero: $W = \oint pdV \neq 0$. On the other hand, since the points A and C lie on one and the same adiabetic ($S_A = S_C$) and the entropy is a single-valued parameter [lit. function] of state, then along this closed-cycle process we have

$$W = Q = \oint T dS = T \int_{(ABC)} dS = 0.$$

The contradiction arising indicates the fact that an isothermal cannot

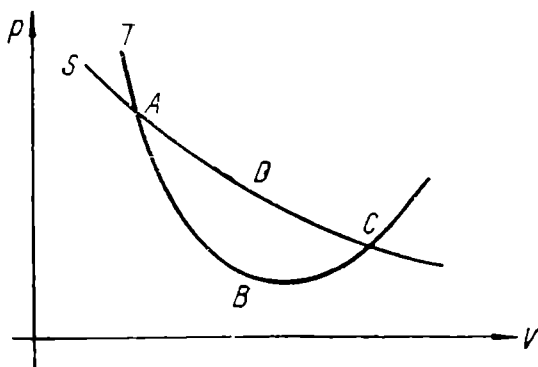


FIG. 48.

intersect twice (or more times) one and the same adiabetic. From this it directly follows that states of equilibrium of a system that can be reached isothermally from a given state are unattainable from it adiabatically (the principle of adiabatic unattainability). In § 13 we have established the principle of adiabatic unattainability in a more general case by surmising that states of an equilibrium system that are reached from a given state whether isothermally or by other means [not involving exchange of heat] cannot be reached adiabatically from the same state.

37. A Pfaffian form in two variables has the form

$$\delta\Pi_2 = X_1(x_1, x_2) dx_1 + X_2(x_1, x_2) dx_2, \quad (1)$$

and the corresponding Pfaff equation is

$$\delta\Pi_2 = X_1 dx_1 + X_2 dx_2 = 0, \quad (2)$$

whence

$$dx_2/dx_1 = -X_1/X_2. \quad (3)$$

If X_1 and X_2 are continuous differentiable and single-valued functions of the independent variables x_1 and x_2 and if $X_2 \neq 0$ over the whole region of variation of these variables, then (3) has always the solution

$$F(x_1, x_2) = C. \quad (4)$$

By differentiating (4) we shall obtain

$$(\partial F/\partial x_1) dx_1 + (\partial F/\partial x_2) dx_2 = 0. \quad (5)$$

By comparing (5) and (2) we establish that the coefficients qualifying dx_1 and dx_2 in these expressions must be proportional, i.e.

$$(\partial F/\partial x_1)/X_1 = (\partial F/\partial x_2)/X_2 = \mu(x_1, x_2).$$

Hence

$$(\partial F/\partial x_1) = \mu X_1, \quad (\partial F/\partial x_2) = \mu X_2$$

and

$$\mu X_1 dx_1 + \mu X_2 dx_2 = \mu \delta\Pi_2 = (\partial F/\partial x_1) dx_1 + (\partial F/\partial x_2) dx_2 = dF,$$

i.e. $\delta\Pi_2$ is always holonomic.

38. Let us consider, as an example of a non-holonomic Pfaffian form, the differential expression

$$\delta\Pi_3 = dx_1 + x_2 dx_3, \quad (1)$$

for which the condition (3.12) is not satisfied, since the left-hand side of (3.12) for (1) is equal to -1 .

The differential equation of the adiabatics will be

$$dx_1 + x_2 dx_3 = 0. \quad (2)$$

Let us choose a function $x_1 = f(x_3)$, otherwise arbitrary but satisfying the following conditions:

$$\begin{aligned} f(x_3^0) &= x_1^0; & f(x_3^1) &= x_1^1; \\ f'(x_3^0) &= -x_2^0; & f'(x_3^1) &= -x_2^1. \end{aligned}$$

This means that the space curve $x_1 = f(x_3)$, $x_2 = -df/dx_3$ will pass through the points x_1^0, x_2^0, x_3^0 , and x_1^1, x_2^1, x_3^1 and will satisfy the adiabatic equation (2) since

$$dx_1 + x_2 dx_3 = (\partial f/\partial x_3) dx_3 - (\partial f/\partial x_3) dx_3 = 0.$$

Thus we have shown by this particular example that, in the case of a non-holonomic Pfaffian form, two arbitrarily chosen points x_1^0, x_2^0, x_3^0 and x_1^1, x_2^1, x_3^1 can be joined by an adiabatic.

Since, as is shown in the course on differential equations, an arbitrary Pfaffian form (3.11) can always be reduced to the form (1), then a similar proposition to above is proved by this in the general case.

39. It has been shown in the problem no. 32 that the mixing of ideal gases of equal temperature is possible by reversible means without communicating heat and by the expenditure of no work. It follows from this that if each gas before the mixing occupied the volume V and had entropy S_1 and S_2 respectively, then after such reversible mixing the entropy of a mixture occupying the volume V will be $S = S_1 + S_2$. Thus the entropy of a mixture of two ideal gases is equal to the sum of the entropies of the two gases separately, calculated on the assumption that each of them occupies the whole volume V (Gibbs' theorem).

In the case of identical gases the pushing together of vessels with such gases does not lead to mixing but to compression of the gas, which, in the presence of a thermostat is accompanied by a release of heat ΔQ and, therefore, by an entropy decrease of value $\Delta Q/T$. Thus Gibbs' theorem is not valid for identical gases. As a consequence of this a variation of entropy in the mixing of two identical gases cannot be obtained as the limiting case of the mixing of two different gases insofar as when different gases are considered Gibbs' theorem is used, which does not apply in the limit case. For identical gases the entropy of the "mixture" after reversible mixing is not equal to the sum of the entropies of the mixing parts calculated on the assumption that each part occupies the volume V , but to the sum of these entropies less the quantity

$$|\Delta Q|/T = W/T = 2\nu RT \log_e (2V/V)/T = 2\nu R \log_e 2,$$

where ν is the number of molecules in each part of the gas before mixing, when the volume of each part is equal to V and that of both parts is $2V$.

The illegitimate application of Gibbs' theorem to the case of identical gases leads to the so-called Gibbs' paradox. The modification of this theorem for identical gases indicated above removes this paradox. In fact, let us imagine a vessel divided into two equal parts by an impermeable diaphragm, and let an ideal gas 1 be found in the left-hand part, and an ideal gas 2 in the right-hand part (Fig. 49). The temperature of the system is maintained constant by means of a thermostat. Let us evaluate the variation of entropy of the system which occurs as a consequence of diffusion when the diaphragm is removed.

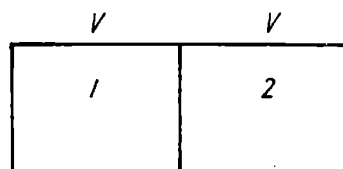


FIG. 49.

The entropy of the system before mixing is equal to the sum of the entropies of the sub-systems:

$$S_I = C_{V_1} \log_e T + R \log_e V + S_{01} + C_{V_2} \log_e T + R \log_e V + S_{02}. \quad (1)$$

According to Gibbs' theorem the entropy of the system after mixing is equal to

$$S_{II} = C_{V_1} \log_e T + R \log_e (2V) + S_{01} + C_{V_2} \log_e T + R \log_e (2V) + S_{02}.$$

The variation of entropy, $S_{II} - S_I$, occurring owing to diffusion will be

$$S_{II} - S_I = 2R \log_e 2$$

and does not depend on the properties of the gases. When applied to identical gases this result leads to the so-called Gibbs' paradox: for identical gases, after the diaphragm has been removed, no thermodynamic process will occur whereas, according to (3), the entropy will increase nevertheless!

This misunderstanding (not a paradox) arises from using Gibbs' theorem for a "mixture" of identical gases for which the theorem is not valid. If we take into account

the fact that in the case of identical gases the entropy after removal of the diaphragm, according to the modified Gibbs' theorem for this case, is equal to

$$S'_{II} = C_{V_1} \log_e T + R \log_e 2V + S_{O1} + C_{V_2} \log_e T + R \log_e 2V + S_{O2} - 2R \log_e 2, \quad (4)$$

then we find that in this case the variation of entropy which results from self-diffusion will be $S'_{II} - S'_I = 0$, i.e. is equal to zero and no paradox arises.

It can be seen from what has been expounded that the widely-held opinion, according to which a complete explanation of Gibbs' paradox cannot be given within the limits of thermodynamics, is erroneous. When arguments are provided to substantiate such an opinion, these are based on two incorrect statements. In the first place it is assumed that Gibbs' paradox can be resolved if it is known how the constant S_0 in the expression for the entropy of an ideal gas depends on the number of particles, N , and, in the second place, it is stated that this dependence cannot be found within the limits of thermodynamics but can be determined only in statistical physics where Gibbs' paradox is resolved. How incorrect the first statement is can be seen from the elucidation of Gibbs' paradox given here, which requires no knowledge of the dependence of S_0 on N . The second statement is also incorrect, since thermodynamics, just as statistical physics, enables us to establish the dependence of S_0 on N , but this does not remove Gibbs' paradox (see problem no. 41). Gibbs' paradox does not arise at all from the fact that in evaluating the variation of entropy for the diffusion of gases we are allegedly ignorant, within the limits of thermodynamics, of the dependence of S_0 on N . It arises from the incorrect application of Gibbs' theorem to the case of identical gases and can be "removed" if such an error is not made.

40. Two different gases comprising ν_1 and ν_2 moles and occupying volumes V_1 and V_2 respectively have, before diffusion, the entropy

$$S_I = \nu_1(C_{V_1} \log_e T + R \log_e V_1 + S_{O1}) + \nu_2(C_{V_2} \log_e T + R \log_e V_2 + S_{O2}),$$

and, after diffusion,

$$S_{II} = \nu_1[C_{V_1} \log_e T + R \log_e (V_1 + V_2) + S_{O1}] + \nu_2[C_{V_2} \log_e T + R \log_e (V_1 + V_2) + S_{O2}].$$

The variation of entropy of the system due to diffusion is equal to

$$S_{II} - S_I = \nu_1 R \log_e (1 + V_2 V_1^{-1}) + \nu_2 R \log_e (1 + V_1 V_2^{-1}).$$

In our case $V_1 = V_2 = 30$ l, $\nu_1 = \nu_2 = 30/11.2$ (since at 2 atm. pressure and 0°C the volume of a gramme-molecule is equal to $22.4/2 = 11.2$ l) we have

$$S_{II} - S_I = 2\nu R \log_e 2 = 2(30/11.2) 2 \log_e 2 \approx 6.9 \text{ cal/degree.}$$

41. From the definition of entropy

$$dS = \delta Q/T \quad (1)$$

it follows that entropy is an additive quantity, proportional to the number N of particles of the system. Therefore if the entropy of one mole of ideal gas at temperature T and pressure p is equal to S_1 , then the entropy of ν moles of such a gas under the same conditions will be $S_\nu = \nu S_1$. We obtain, from (1), for the entropy of one mole

$$S_1 - S_{01} = C_V \log_e (T/T_0) + R \log_e (V/V_0),$$

and we have for ν moles

$$S_\nu - S_{0\nu} = \nu C_V \log_e (T/T_0) + \nu R \log_e (\nu V/\nu V_0).$$

Thus

$$S_\nu = \nu C_V \log_e T + \nu R \log_e (\nu V) - \nu C_V \log_e T_0 - \nu R \log_e (\nu V_0) + \nu S_{01},$$

and the additivity of entropy leads to the following dependence of the constant b_ν on ν :

$$b_\nu = -\nu R \log_e (\nu V_0) - \nu (C_V \log_e T_0 - S_{01}).$$

As for a given gas for fixed values of T_0 and p_0 the thermal capacity C_V , the entropy S_0 and the volume V_0 have determined values while $\nu = N/N_0$, then

$$b_\nu = -\nu R \log_e N + BN, \quad (2)$$

where the constant B is equal to

$$B = \frac{1}{N_0} [-C_V \log_e T_0 + S_{01} - R \log_e (V_0/N_0)].$$

Therefore

$$S_\nu = \nu C_V \log_e T + \nu R \log_e (\nu V) - \nu R \log_e N + BN \quad (3)$$

and

$$S_1 = C_V \log_e T + R \log_e V - R \log_e N + BN. \quad (4)$$

We have found the dependence (2) of the constant b_ν on the number of particles N by purely thermodynamic means. Statistical physics leads exactly to the same dependence.

The expression for the entropy (4) implies that entropy increases for the diffusion of two gases independently of their nature, and therefore leads to Gibbs' paradox if the variation of entropy for the mixing of two portions of one and the same gas is found, as in the case of different gases, by using Gibbs' theorem. In fact, let us evaluate the variation of entropy for the diffusion of gases A and B (one mole of each) after the removal of a diaphragm separating them. The temperature of the system is maintained constant by means of a thermostat; the volume of each gas before the removal of the diaphragm is equal to V .

The case of different gases. The entropy of the system before diffusion begins is equal to

$$S = C_{VA} \log_e T + R \log_e V - R \log_e N_A + BN_A + C_{VB} \log_e T + R \log_e V - R \log_e N_B + BN_B.$$

According to Gibbs' theorem the entropy after diffusion (see problem no. 39) will be

$$S' = C_{VA} \log_e T + R \log_e (2V) - R \log_e N_A + BN_A + C_{VB} \log_e T + R \log_e (2V) - R \log_e N_B + BN_B.$$

The variation of entropy as a result of diffusion is equal to

$$S' - S = 2R \log_e 2.$$

The case of identical gases. The entropy before the removal of the diaphragm is

$$S = C_V \log_e T + R \log_e V - R \log_e N + BN + C_V \log_e T + R \log_e V - R \log_e N + BN,$$

and after removal of the diaphragm, according to Gibbs' theorem, the entropy is equal to

$$S' = C_V \log_e T + R \log_e (2V) - R \log_e N + BN + C_V \log_e T + R \log_e (2V) - R \log_e N + BN.$$

The variation of entropy as a result of removal of the diaphragm will be

$$S' - S = 2R \log_e 2.$$

Thus, even by using an expression for the entropy where the dependence of S_0 on N is explicit, Gibbs' paradox is not eliminated. This is due to the incorrect application of Gibbs' theorem in evaluating S' in the case of identical gases when the theorem is not valid. The entropy after removal of the diaphragm in the case of identical gases must

be found not by Gibbs' theorem, but by using for the entropy the expression (3) which satisfies the additivity property. In fact, after removal of the diaphragm we have two moles of one and the same gas ($\nu = 2$, the total number of particles is equal to $2N$), and therefore, according to (3):

$$S^* = 2C_V \log_e T + 2R \log_e 2V - 2R \log_e 2N + 2BN$$

so that $S^* - S = 0$.

It can be seen from what has been expounded that Gibbs' paradox arises from misunderstanding: owing to neglect of the qualitative saltus in the passage from different to identical gases. This is why numerous investigations devoted to discussing Gibbs' paradox have led to no result whatsoever which could provide a definitive clarification of this "made-up" predicament. By modifying Gibbs' theorem for the case of mixing of two portions of one and the same gas (see problem no. 39) or else by evaluating the entropy after the mixing of such gases, without having recourse to Gibbs' theorem, but using for the entropy the thermodynamic expression (3), which satisfies the additivity property, we can, within the limits of thermodynamics proper, avoid the error (Gibbs' paradox) in evaluating the variation of entropy in the case of mixing of identical gases.

42. According to Boltzmann's principle $S = f(W)$. If a system consists of two parts, then $S_1 = f(W_1)$, $S_2 = f(W_2)$ and, on the basis of the additivity of entropy,

$$S = S_1 + S_2 = f(W_1) + f(W_2) = f(W).$$

For independent systems $W = W_1 W_2$ and therefore we obtain, for determining $f(W)$, the functional equation $f(W_1) + f(W_2) = f(W_1 W_2)$. By differentiating it with respect to W_1 and W_2 we shall have

$$f'(W_1) = f'(W_1 W_2) W_2,$$

$$f'(W_2) = f'(W_1 W_2) W_1,$$

whence

$$f'(W_1)/f'(W_2) = W_2/W_1, \quad W_1 f'(W_1) = W_2 f'(W_2) = \text{const},$$

and, after integrating

$$f(W) = \text{const.} \log_e W$$

or

$$S = k \log_e W.$$

The constant is obtained by applying this equation to some particular case, for example, to an ideal gas; it is found to be equal to Boltzmann's constant

$$k = 1.38 \times 10^{-16} \text{ erg/degree.}$$

43. The total entropy of the two bodies will vary by the quantity

$$\Delta S = (1/300) - (1/301) = (1/9) \times 10^{-4} \text{ erg/degree.}$$

According to Boltzmann's principle

$$\Delta S = k \log_e (W_2/W_1),$$

where W_1 is the probability of the initial state of the two gases, and W_2 is the probability of their final state in the process considered; therefore

$$W_2 = W_1 \exp (\Delta S/k) = W_1 \exp (10^{-4}/9 \times 1.38 \times 10^{-16}) = W_1 \exp (10^{12}/12),$$

i.e. the probability of the second state exceeds by an inconceivably large number of times the probability of the first state and, when the two bodies are in contact, heat flows from the hot to the cold body practically in all cases. In the average, out of $W_2/W_1 \approx 10 \times 10^{10}$ cases only once will heat flow from the cold to the hot body. We

see that in practice the probability of the direction of heat flow expected from thermodynamics does not differ from certainty.

The result, however, would be different for the flow of a considerably smaller quantity of heat than 1 erg. In the case when $\Delta Q = 1.2 \times 10^{-9}$ erg we obtain

$$W_2/W_1 = e = 2.7,$$

i.e. the flow of such a quantity of heat from a cold to a hot body will still occur more rarely than the flow in the opposite direction, but the frequencies of these flows will be of the same order.

$$44. \delta Q = dU + \delta W, \delta Q_{n-st} = -dU + \delta W_{n-st}$$

For the entire closed-cycle process the quantity

$$\delta Q + \delta Q_{n-st} = \delta W + \delta W_{n-st}$$

is negative, since in the opposite case work would be accomplished $\delta W + \delta W_{n-st} > 0$ at the expense of heat $\delta Q + \delta Q_{n-st} > 0$ without any compensation. Thus $-\delta W > \delta W_{n-st}$; this means that the work of the system in the (2 - 1) quasi-static process, equal to $\delta W' = -\delta W$, is greater than the work of the system in the (2 - 1) non-static process.

The consideration of the given cycle shows that in the presence of non-static processes a closed-cycle process with non-zero work is possible with a single thermostat. Work over such a cycle will always be negative; this means that it is carried out by external bodies and provides an increase in the internal energy of the thermostat.

Here is a manner of accomplishing such a cycle in practice. Let the system have initially the temperature T of the thermostat (the state A in Fig. 50). Let us insulate the system and let it expand adiabatically to reach the temperature T_1 (the state B). Let us then establish thermal contact of the system with the thermostat. The temperature of the system will rise non-statically to the previous value T (the segment BC in the figure). By compressing the system isothermally we can return it to its initial state. It can be seen from the direction in which the contour is described on the diagram that the work over a cycle will be negative. (The state 1 in Fig. 12 corresponds to the state C in Fig. 50, the state 2 to the state B , the 1-2 quasi-static transition in Fig. 12 to the CAB transition in Fig. 50, and the 2-1 non-static transition to the BC transition.)

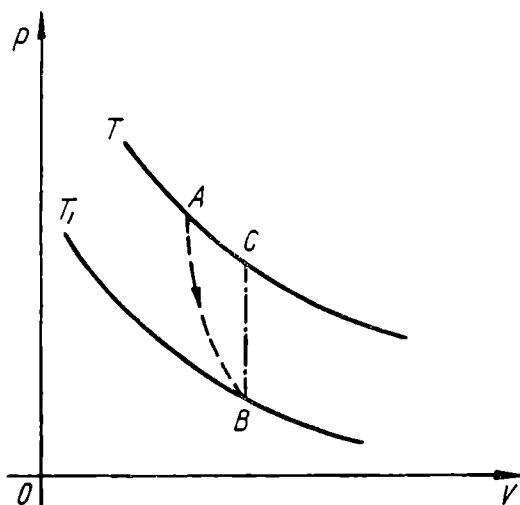


FIG. 50.

will be negative. (The state 1 in Fig. 12 corresponds to the state C in Fig. 50, the state 2 to the state B , the 1-2 quasi-static transition in Fig. 12 to the CAB transition in Fig. 50, and the 2-1 non-static transition to the BC transition.)

45. $\delta Q = dU + p dV = C_V dT + [(\partial U / \partial V)_T + p] dV = C_V dT + T(\partial p / \partial T)_V dV$. But $(\partial p / \partial T)_V = \alpha / \beta$ and therefore

$$\delta Q = C_V dT + T(\alpha / \beta) dV.$$

In the adiabatic process ($\delta Q = 0$)

$$dT = -T\alpha C_V^{-1} \beta^{-1} dV.$$

From this it can be seen that when water is compressed adiabatically ($dV < 0$) in the interval $0^\circ < t < 4^\circ\text{C}$ where α for water is negative, it will cool ($dT < 0$).

46. Let us consider Carnot's cycle (Fig. 9) with water as the working fluid for $T_1 = 283^\circ\text{K} = 10^\circ\text{C}$ and $T_2 = 277^\circ\text{K} = 4^\circ\text{C}$.

We have for a cycle

$$\oint T^{-1}\delta Q = 0,$$

or

$$\Delta S_{12} + \Delta S_{23} + \Delta S_{34} + \Delta S_{41} = 0.$$

But

$$\Delta S_{12} = Q_1/T_1 = Q_1/283 > 0, \quad \Delta S_{23} = \Delta S_{41} = 0.$$

From the equation of the first law

$$\delta Q = C_V dT + T(\alpha/\beta) dV$$

we obtain for the isothermal process of water at 4°C , when $\alpha = 0$, $\delta Q = 0$, and therefore $\Delta S_{34} = 0$. Thus

$$\oint T^{-1}\delta Q = Q_1/283 \neq 0,$$

which contradicts the second law. Therefore the temperature of 4°C cannot be reached for water by cooling it by means of adiabatic expansion.

47. It can be seen from the solution of problem no. 46 that it is impossible to accomplish Carnot's cycle with temperatures 6°C and 2°C when water is taken as the working fluid. This resolves the contradiction shown in the problem.

48. The fundamental equation of thermodynamics

$$TdS = dU + pdV$$

applied to the isothermal cycle *abcdeca* (Fig. 51) gives

$$T \oint dS = \oint dU + \oint pdV.$$

But $\oint dS = 0$ and $\oint dU = 0$, and therefore $\oint pdV = 0$, whence it follows that the areas 1 and 2 are equal.

49. $S = \int T^{-1}(dU + pdV) = \int T^{-1}[C_V dT + T(\partial p/\partial T)_V dV] = \int T^{-1}C_V dT + \int (\partial p/\partial T)_V dV$. From $p = RT(V-b)^{-1} - \alpha V^{-2}$ the derivative $(\partial p/\partial T)_V = R(V-b)^{-1}$ and therefore

$$S = \int T^{-1}C_V dT + R \log_e (V-b) + S_0.$$

As C_V depends little on temperature then

$$S = C_V \log_e T + R \log_e (V-b) + S_0.$$

For an adiabatic process $S = S_0 = \text{const}$, and therefore

$$T(V-b)^{R/C_V} = \text{const}.$$

50. $C_p - C_V = [(\partial U/\partial V)_T + p](\partial V/\partial T)_p = T(\partial p/\partial T)_V (\partial V/\partial T)_p = -T(\partial p/\partial T)_V^2 / (\partial p/\partial V)_T$. From $p = RT(V-b)^{-1} - \alpha V^{-2}$ we find

$$(\partial p/\partial T)_V = R/(V-b)$$

$$(\partial p/\partial V)_T = -RT(V-b)^{-2} + 2\alpha V^{-3}.$$

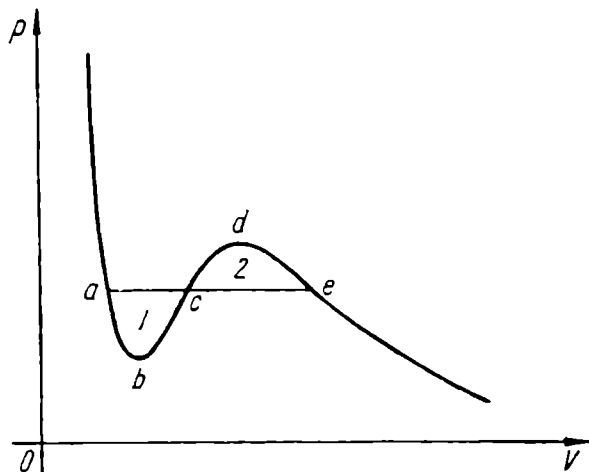


FIG. 51.

Thus

$$C_p - C_v = R / [1 - 2a(V - b)^2 / RTV^3].$$

For a gas of low density, by retaining only the terms linear with respect to a and b , we shall obtain

$$C_p - C_v = R(1 + 2aR^{-1}T^{-1}V^{-1}).$$

51. According to (3.50)

$$T(\partial A / \partial T)_a = (\partial U / \partial a)_T + A. \quad (3.50)$$

In the case of a magnetic substance $\delta W = -HdM$ and therefore $A = -H$, $a = M$ and, consequently,

$$-T(\partial H / \partial T)_M = (\partial U / \partial M)_T - H.$$

For an ideal paramagnetic substance the internal energy depends only on temperature and therefore

$$(\partial U / \partial M)_T = 0 \quad \text{and} \quad (\partial H / \partial T)_M = H/T,$$

whence it directly follows that

$$M = f(H/T). \quad (1)$$

The form of the function $f(H/T)$ cannot be determined by thermodynamics. For paramagnetic gases the permeability does not depend on H , and therefore we immediately obtain from (1) Curie's law

$$M = CH/T,$$

where C is Curie's constant.

52. From $M = \kappa H$ and Curie's law $\kappa = C/T$ we obtain $M = CH/T$. According to (3.50) we obtain for a magnetic substance ($A = -H$, $a = M$)

$$-T(\partial H / \partial T)_M = (\partial U / \partial M)_T - H.$$

However, $(\partial H / \partial T)_M = M/C$ and therefore $(\partial U / \partial M)_T = 0$, i.e. the internal energy of a paramagnetic substance obeying Curie's law does not depend on the magnetization M (nor on the magnetic field H) but depends only on temperature:

$$U = U(T).$$

Such a paramagnetic substance is called an ideal paramagnetic substance.

53. From (2.7) and (3.50) we have

$$C_A - C_a = T(\partial A / \partial T)_a (\partial a / \partial T)_A,$$

where A and a are associated quantities so that

$$\delta W = A da.$$

The stretching work $\delta W = -f dl = -E s dl$, where s is the area of the rod cross-section and E is the stress. Hence $a = l$, $A = -Es$.

Thus

$$C_E - C_\lambda = -Tsl (\partial E / \partial T)_\lambda (\partial \lambda / \partial T)_E,$$

where $\lambda = dl/l$ is the strain and l is the rod length.

54. By putting in the formula

$$C_A - C_a = T(\partial A / \partial T)_a (\partial a / \partial T)_A$$

$a = D$ and $A = -E/4\pi$, we shall obtain

$$C_E - C_D = - (T/4\pi) (\partial E / \partial T)_D (\partial D / \partial T)_E.$$

But

$$(\partial E / \partial T)_D = [\partial(D/\epsilon) / \partial T]_D = - (E/\epsilon) \partial \epsilon / \partial T; \quad (\partial D / \partial T)_E = E \partial \epsilon / \partial T,$$

and therefore

$$C_E - C_D = (TE^2/4\pi e) (\partial \varepsilon / \partial T)^2 > 0,$$

and hence

$$C_E > C_D.$$

55. From the expression of the differential of entropy

$$dS = \delta Q/T = T^{-1} [C_V dT + T(\partial p / \partial T)_V dV]$$

we find

$$[\partial(C_V/T) / \partial V]_T = [\partial(\partial p / \partial T)_V / \partial T]_V,$$

or

$$\partial C_V / \partial V = T \partial^2 p / \partial T^2.$$

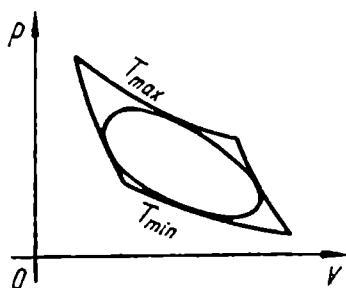


FIG. 52.

From this it can be seen that if p depends linearly on the temperature T , then $(\partial C_V / \partial V)_T = 0$, i.e. C_V does not depend on volume. Such is the C_V of an ideal gas and of a van der Waals' gas, since in both these cases the pressure is a linear function of temperature.

As regards C_p , it depends on V in a van der Waals' gas.

56. Let, in a certain cycle, T_{\max} be the maximum temperature at which the system receives heat, and T_{\min} be the minimum temperature at which it cedes heat (Fig. 52). The efficiency of this cycle is equal to

$$\eta = (W/Q_1) = (Q_1 - Q_2) / Q_1,$$

where $Q_P = \int_P \delta Q = \int_P |\delta Q|$ is the quantity of heat obtained over a cycle (the letter P qualifying the integrals indicates that the integral is taken over those sections of the cycle for which δQ is positive); $Q_N = \int_N |\delta Q| = -\int_N \delta Q$ is the quantity of heat ceded

by the working body over a cycle (this indicated by the letter N). According to Clausius's equality

$$\oint \delta Q/T = \int_P \delta Q/T + \int_N \delta Q/T = \int_P |\delta Q|/T - \int_N |\delta Q|/T = 0,$$

whence

$$\int_P |\delta Q|/T = \int_N |\delta Q|/T.$$

But

$$\begin{aligned} \int_P |\delta Q|/T &\geq T_{\max}^{-1} \int_P |\delta Q| = Q_1/T_{\max}; \\ \int_N |\delta Q|/T &\leq T_{\min}^{-1} \int_N |\delta Q| = Q_2/T_{\min}, \end{aligned}$$

and therefore

$$Q_1/T_{\max} \leq Q_2/T_{\min},$$

whence

$$Q_2/Q_1 \geq T_{\min}/T_{\max}, \quad (Q_2 - Q_1)/Q_1 \geq (T_{\min} - T_{\max})/T_{\max}$$

and

$$\eta = (Q_1 - Q_2)/Q_1 \leq (T_{\max} - T_{\min})/T_{\max} = \eta_{\text{Carnot}}.$$

Thus Carnot's cycle has the largest efficiency in comparison with all other cycles under the same temperature limits.

57. By definition

$$\eta = W/Q_1 = (Q_1 - Q_2)/Q_1,$$

but

$$Q_1 = Q_{12} + Q_{41} = RT_1 \log_e (V_2/V_1) + C_V(T_1 - T_2),$$

$$Q_2 = |Q_{23}| + |Q_{34}| = C_V(T_1 - T_2) + RT_2 \log_e (V_2/V_1).$$

Thus

$$\begin{aligned} \eta &= R(T_1 - T_2) \log_e (V_2/V_1) / [RT_1 \log_e (V_2/V_1) + C_V(T_1 - T_2)] = \\ &= (T_1 - T_2) / [T_1 + C_V(T_1 - T_2) / R \log_e (V_2/V_1)]. \end{aligned}$$

Hence it can be seen that

$$\eta < (T_1 - T_2)/T_1 = \eta_{\text{Carnot}},$$

i.e. the efficiency of Stirling's cycle is smaller than that of Carnot's cycle. (The shaded area in Fig. 53 corresponds to Carnot's cycle.)

58. The work in internal-combustion engines is carried out not at the expense of heat from without, but at the expense of the internal energy of the working substance (the gas mixture). In Otto's cycle the gas mixture sucked into the cylinder is adiabatically compressed (1-2), ignited by a spark, burns isochorically (2-3), expands adiabatically (3-4) and is ejected to the atmosphere (4-1).

The efficiency of the cycle is $\eta = W/Q_1$, where W is the work over a cycle and Q_1 is the quantity of heat liberated in the cylinder. It is evident that W is equal to the difference of the works along the adiabatics. By assuming the gas mixture to be an ideal gas we shall have

$$W = C_V(T_3 - T_4) - C_V(T_2 - T_1),$$

$$Q_1 = C_V(T_3 - T_2),$$

and

$$\eta = 1 - (T_4 - T_1) / (T_3 - T_2).$$

Let us express η in terms of ε . From the equation of the adiabatic $TV^{\gamma-1} = \text{const}$ we find

$$T_3 = T_4(V_4/V_3)^{\gamma-1} = T_4\varepsilon^{\gamma-1} \quad \text{and} \quad T_2 = T_1(V_1/V_2)^{\gamma-1} = T_1\varepsilon^{\gamma-1}.$$

Thus $\eta = 1 - \varepsilon^{1-\gamma}$. In practice $\varepsilon = 3.5-7$ and $\eta \approx 25\%$.

59. In Diesel's cycle: (1-2) is adiabatic compression of atmospheric air, (2-3) is isobaric expansion (injection of gas mixture and its burning), (3-4) is adiabatic expansion and (4-1) is cooling at constant volume.

The work over a cycle is equal to

$$W = W_{12} + W_{23} + W_{34} = C_V(T_1 - T_2) + R(T_3 - T_2) + C_V(T_3 - T_4).$$

The heat liberated in the cylinder during a cycle is equal to

$$Q_1 = Q_{23} = C_p(T_3 - T_2).$$

Thus

$$\begin{aligned} \eta &= W/Q_1 = [C_V(T_1 - T_2) + (C_p - C_V)(T_3 - T_2) + C_V(T_3 - T_4)] / C_p(T_3 - T_2) \\ &= 1 - (1/\gamma)(T_4 - T_1)/(T_3 - T_1), \end{aligned}$$

or

$$\eta = 1 - (1/\gamma)(T_1/T_2)[(T_4/T_1) - 1] / [(T_3/T_2) - 1].$$

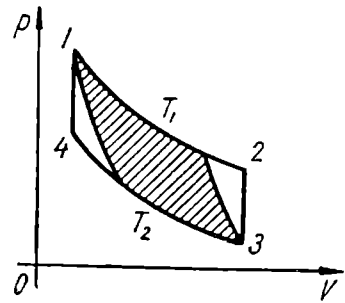


FIG. 53.

But

$$\begin{aligned}T_2 V_2^{\gamma-1} &= T_1 V_1^{\gamma-1} \text{ and } (T_1/T_2) = (V_2/V_1)^{\gamma-1} = \epsilon^{1-\gamma}; \\T_2/V_2 &= T_3/V_3 \quad \text{and } (T_3/T_2) = (V_3/V_2) = \varrho; \\T_3 V_3^{\gamma-1} &= T_4 V_1^{\gamma-1}, \quad T_2 V_2^{\gamma-1} = T_1 V_1^{\gamma-1},\end{aligned}$$

whence

$$T_4/T_1 = (T_3/T_2)(V_3/V_2)^{\gamma-1} = \varrho \varrho^{\gamma-1} = \varrho^\gamma$$

and finally

$$\eta = 1 - (1/\gamma \epsilon^{\gamma-1})(\varrho^\gamma - 1)/(\varrho - 1).$$

60. By definition: $\eta = (Q_1 - Q_2)/Q_1 = W/Q_1$, $\varphi = Q_1/W$, $\psi = Q_2/W$. The evaluation of η for Carnot's cycle gives $\eta = (T_1 - T_2)/T_1$. Therefore for the inverse cycle we find without difficulty $\varphi = T_1/(T_1 - T_2)$ and $\psi = T_2/(T_1 - T_2)$. It can easily be seen that a variation of the upper temperature affects both φ and ψ as well as η to a smaller extent than does a variation of the lower temperature

$$\partial\varphi/\partial T_1 = -T_2/(T_1 - T_2)^2, \quad \partial\varphi/\partial T_2 = T_1/(T_1 - T_2)^2$$

and

$$\begin{aligned}|\partial\varphi/\partial T_1| &< |\partial\varphi/\partial T_2|; \quad \partial\psi/\partial T_1 = -T_2/(T_1 - T_2)^2, \\ \partial\psi/\partial T_2 &= T_1/(T_1 - T_2)^2,\end{aligned}$$

whence we observe that

$$\partial\varphi/\partial T_1 = \partial\psi/\partial T_1, \quad \partial\varphi/\partial T_2 = \partial\psi/\partial T_2 \text{ and } |\partial\psi/\partial T_1| < |\partial\psi/\partial T_2|.$$

61. By definition $n_- = Q/Q_1$, where $Q = Q_2 + Q'_2$. For a heat engine $W = Q_1 - Q_2$, while for a heat pump the same work is equal to $W = Q'_2 - Q_0$. Therefore $Q_1 - Q_2 = Q'_2 - Q_0$, $Q = Q_2 + Q'_2 = Q_1 + Q_0$ and $n_- = 1 + (Q_0/Q_1) = 1 + (Q_0/W)(W/Q_1) = 1 + \psi\eta = 1 + (\varphi - 1)\eta$. Since (see the solution of problem no. 60 and take account of the fact that in the case given the heat pump works between the temperature T_0 and T_2) $\eta = (T_1 - T_2)/T_1$ and $\psi = T_0/(T_2 - T_0)$, then

$$n_- = T_2(T_1 - T_0)/T_1(T_2 - T_0).$$

62. By definition $n_+ = Q_1/Q = Q_1/(Q_2 + Q'_2)$. However, $\eta = (Q_2 - Q_0)/Q_2 = W/Q_2 = (T_2 - T_0)/T_2$,

$$\varphi = Q_1/W = T_1/(T_1 - T_2), \quad \psi = Q'_2/W = T_2/(T_1 - T_2),$$

whence

$$Q_2 = W/\eta, \quad Q_1 = W\varphi, \quad Q'_2 = W\psi.$$

Therefore

$$n_+ = \varphi\eta/(1 + \psi\eta) = \varphi\eta/[1 + (\varphi - 1)\eta]$$

or

$$n_+ = T_1(T_2 - T_0)/T_2(T_1 - T_0).$$

63. Rigorously speaking, no real phenomenon can be fully reversible, since the set of conditions under which it occurs can never be repeated in the infinite universe. This, however, indicates that the universe has a past and a future. The reversibility of physical phenomena has not an absolute but a relative character. A dialectical unity of reversibility and irreversibility exists in nature. The fact that in the equations of mechanics the time occurs raised to the second power and the sign of time changes nothing, indicating seemingly the reversibility of natural phenomena, is evidence of the fact that these equations, as all laws of physics, represent real phenomena not completely but unilaterally.

64. States of a system are characterized macroscopically by the value of such parameters as pressure, volume, density etc. Microscopically, however, the state of a mole-

cular system is determined by the set of molecules in various states (with given coordinates and momenta). A permutation of particles with respect to their states modifies the micro-state but not the macro-state (here the quantum properties of particles are disregarded). The number of different micro-states giving rise to a given macro-state is called the thermodynamic probability of the given macro-state. The entropy S of the system in a certain state is connected with the thermodynamic probability W of this state by Boltzmann's relation $S = k \log_e W$.

In Plotkin's paper it is shown that in the case of an infinite universe the sets of different micro-states that characterize different macro-states have the same power, namely the power of continuum. As a consequence of this all macro-states of the system are here equivalent, and therefore there is no tendency to transition from less probable to more probable states. Consequently the results of thermodynamics and statistical physics on thermodynamic equilibrium are inapplicable to the infinite universe.

Let us consider a system of an enumerable set of equal particles (for example, molecules). Each of the possible micro-states of the system can be assigned by means of a sequence of positive integers $n_1, n_2, \dots, n_i, \dots$, where n_i is the number of particles in the i -th state. The number W of all micro-states giving rise to a given macro-state is equal to

$$W = N! / \prod_i n_i!$$

where $N = \sum_i n_i$. By Stirling's formula for $N \gg 1$

$$N! = N^N e^{-N},$$

and therefore

$$W = N^N / \prod_i n_i^{n_i} = \prod_i (N/n_i)^{n_i}.$$

By putting $N/n_i = 2^{\alpha_i}$, where $\alpha_i > 0$, since $N/n_i > 1$, we shall obtain

$$W = 2^{\sum \alpha_i n_i}. \quad (1)$$

Since $\sum \alpha_i n_i$ is an enumerable infinity, it follows from (1), in accordance with a known proposition of set theory, that W is an infinity of higher power, namely of the power of continuum.

65. Any state in the region α between the adiabatic and the iso-energy line can be reached from C_0 by means of non-equilibrium expansion: any state in the region β between the adiabatic and the isochoric can be reached by means of non-equilibrium adiabatic compression; finally all states in the region γ between the isochoric and the iso-energy line can be reached from C_0 by a combination of non-equilibrium adiabatic expansion and non-equilibrium adiabatic compression. Any of the states of the region C having entropy $S < S_0$ cannot be reached adiabatically (states absolutely unattainable adiabatically from C_0). For the transition from C_0 to C we need to abstract from the body a certain quantity of heat. If the heat abstracted from the body could be converted into work without compensation then, by including in the system considered a mechanism for accomplishing such a conversion, we would arrive at the result that any state C is always attainable adiabatically from any other arbitrary state C_0 . From this it can be seen that the absolute adiabatic unattainability is a consequence

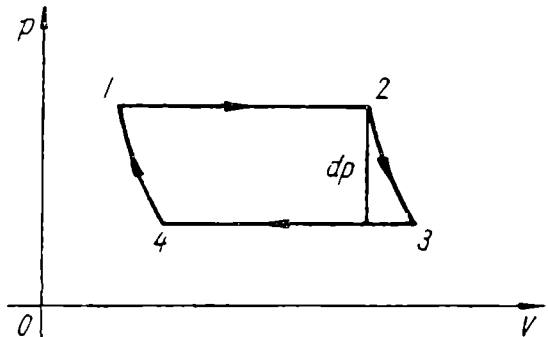


FIG. 54.

of both propositions of the second law of thermodynamics, in contrast to the relative (quasi-static) adiabatic unattainability, which is a consequence of the impossibility of a perpetual motor of the second kind (the first proposition of the second law).

66. Let us consider a Carnot's cycle in which the working substance is a system of liquid and saturated vapour. Let us represent this cycle on the V, p diagram (Fig. 54). During the section 1-2 the system expands isothermally (at the temperature T), a unit mass of liquid being converted into vapour; the pressure does not vary. The quantity of heat taken from the heater is equal to $Q_1 = \lambda$. In the adiabatic expansion 2-3 temperature and pressure decrease by dT and dp respectively. In the isothermal compression 3-4 the quantity of heat Q_2 is ceded to the refrigerator, and in the adiabatic compression 4-1 the temperature rises to T .

The work during one cycle is equal to $Q - Q_2 = (v_2 - v_1)dp$, where v_2 and v_1 are the specific volumes of vapour and liquid respectively. Therefore

$$\eta = (Q_1 - Q_2)/Q_1 = (v_2 - v_1)\lambda^{-1}dp.$$

We have, however, for Carnot's cycle

$$\eta = [T - (T - dT)]/T = dT/T,$$

and therefore

$$\lambda^{-1}(v_2 - v_1)dp = T^{-1}dT.$$

Thus we obtain the Clapeyron-Clausius equation

$$dp/dT = \lambda T^{-1}(v_2 - v_1)^{-1},$$

which determines the variation of saturated-vapour pressure with a variation of temperature.

67. We shall accomplish Carnot's cycle with a reversible galvanic cell, by letting it work at first isothermally, then adiabatically, and then, by letting current from an external source flow through it, we shall accomplish work on it also isothermally and adiabatically.

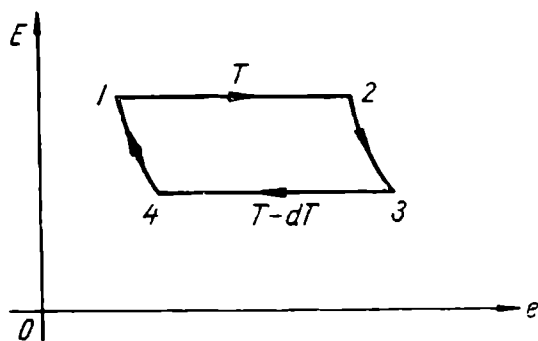


FIG. 55.

On a diagram having axes e (the charge flowing through the cell) and \mathcal{E} (the e.m.f. of the cell) the cycle will have the form shown in Fig. 55. The quantity of heat taken from the heater along the isothermal 1-2 will be $Q_1 = U_2 - U_1 + W_1$, where the isothermal work is $W = e\mathcal{E}$ while the variation of internal energy $U_2 - U_1$ is equal to the heat effect of the chemical reaction in the cell (if the cell did not accomplish work) $U_2 - U_1 =$

$= -qe$ (q is the heat effect per unit flowing charge), so that $Q_1 = e\mathcal{E} - qe$. In the adiabatic work 2-3 the e. m. f. of the cell decreases by $d\mathcal{E}$, and temperature will also vary. Then by letting current from an external source flow through the element, we shall complete this Carnot cycle. The work during a cycle is equal to the area of the cycle on the diagram $e d\mathcal{E}$, and therefore

$$\eta = (Q_1 - Q_2)/Q_1 = e d\mathcal{E}/(e\mathcal{E} - qe) = d\mathcal{E}/(\mathcal{E} - q).$$

We have, however, for Carnot's cycle,

$$\eta = [T - (T - dT)]/T = dT/T,$$

and therefore

$$d\mathcal{E}/(\mathcal{E} - q) = dT/T,$$

whence we obtain Helmholtz's equation

$$\mathcal{E} = q + T(\partial \mathcal{E} / \partial T),$$

which is discussed in § 23.

68. Let us consider a cycle consisting of an isochoric, an isobaric and an isothermal (Fig. 56). According to the first law, the work W during a cycle is equal to $W = Q_1 + Q_2 - Q_3$, where

$$Q_1 = C_V dT, \quad Q_2 = l dV = l(\partial V / \partial T)_p dT,$$

$$Q_3 = C_p dT, \text{ and } l = (\partial U / \partial V)_T + p$$

is the latent heat of isothermal expansion. It can be seen from the figure that

$$ab = (\partial p / \partial T)_V dT, \quad ac = (\partial V / \partial T)_p dT,$$

and

$$W = (1/2)ab \times ac = (1/2) (\partial p / \partial T)_V (\partial V / \partial T)_p (dT)^2.$$

Thus

$$(1/2) (\partial p / \partial T)_V (\partial V / \partial T)_p (dT)^2 = C_V dT + l(\partial V / \partial T)_p dT - C_p dT,$$

whence

$$C_p - C_V = l(\partial V / \partial T)_p,$$

or

$$C_p - C_V = [(\partial U / \partial V)_T + p] (\partial V / \partial T)_p.$$

69.

$$C_p - C_V = T(\partial p / \partial T)_V (\partial V / \partial T)_p,$$

but

$$C_p = T(\partial S / \partial T)_p, \quad C_V = T(\partial S / \partial T)_V,$$

and therefore

$$(\partial S / \partial T)_p - (\partial S / \partial T)_V = (\partial p / \partial T)_V (\partial V / \partial T)_p$$

or

$$(\partial S / \partial V)_p (\partial V / \partial T)_p - (\partial S / \partial p)_V (\partial p / \partial T)_V = (\partial p / \partial T)_V (\partial V / \partial T)_p$$

and

$$(\partial T / \partial p)_V (\partial S / \partial V)_p - (\partial T / \partial V)_p (\partial S / \partial p)_V = 1. \quad (1)$$

We could replace p and V in the relation (1) by other conjugate quantities A and a , and we would have

$$(\partial T / \partial A)_a (\partial S / \partial a)_A - (\partial T / \partial a)_A (\partial S / \partial A)_a = 1. \quad (2)$$

The quantities T and S are also conjugate, and therefore if we replace T , in (2), by A_1 and S by a_1 , we shall obtain

$$(\partial A_1 / \partial A)_a (\partial a_1 / \partial a)_A - (\partial A_1 / \partial a)_A (\partial a_1 / \partial A)_a = 1. \quad (3)$$

By putting here $A = T$, $a = S$ and $A_1 = p$, $a_1 = V$ we shall have

$$(\partial p / \partial T)_S (\partial V / \partial S)_T - (\partial p / \partial S)_T (\partial V / \partial T)_S = 1.$$

This relation could have been obtained directly from (1) by carrying out in it the substitution

$$T \longrightarrow p \quad S \longrightarrow V$$

and

$$V \longrightarrow S \quad p \longrightarrow T.$$

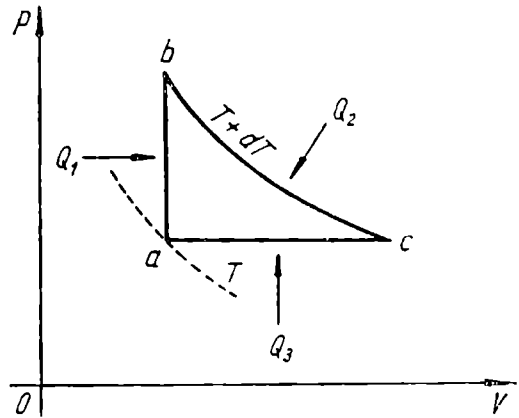


FIG. 56.

$$\begin{aligned}
 70. C_p - C_V &= T(\partial p / \partial T)_V (\partial V / \partial T)_p = T(\partial p / \partial T)_V / (\partial T / \partial V)_p = \\
 &= T(\partial p / \partial T)_V^2 / [(\partial T / \partial V)_p (\partial p / \partial T)_V]. \text{ By using the identity} \\
 &(\partial T / \partial V)_p (\partial p / \partial T)_V (\partial V / \partial p)_T = -1,
 \end{aligned}$$

we find

$$C_p - C_V = -T(\partial p / \partial T)_V^2 / (\partial p / \partial V)_T.$$

However,

$$p = -(\partial F / \partial V)_T, \quad (\partial p / \partial T)_V = -\partial^2 F / \partial T \partial V, \quad (\partial p / \partial V)_T = -(\partial^2 F / \partial V^2)_T,$$

and therefore

$$C_p - C_V = T(\partial^2 F / \partial T \partial V)^2 / (\partial^2 F / \partial V^2)_T.$$

71. By using the properties of Jacobians we have

$$\begin{aligned}
 (\partial p / \partial V)_S &= \partial(p, S) / \partial(V, S) = [\partial(p, S) / \partial(p, T)] [\partial(p, T) / \partial(V, S)] = \\
 &= (\partial S / \partial T)_p [\partial(p, T) / \partial(V, T)] [\partial(V, T) / \partial(V, S)] = \\
 &= (\partial S / \partial T)_p (\partial p / \partial V)_T (\partial T / \partial S)_V = (C_p / C_V) (\partial p / \partial V)_T.
 \end{aligned}$$

72. Similarly to problem no. 71 we have

$$\begin{aligned}
 (\partial T / \partial V)_S &= \partial(T, S) / \partial(V, S) = [\partial(T, S) / \partial(V, T)] [\partial(V, T) / \partial(V, S)] = \\
 &= -(\partial S / \partial V)_T / (\partial S / \partial T)_V.
 \end{aligned}$$

$$\begin{aligned}
 73. F(T, V) &= U - TS = C_V T + U_0 - T(C_V \log_e T + R \log_e V + S_0) = \\
 &= C_V T(1 - \log_e T) - RT \log_e V - TS_0 + U_0;
 \end{aligned}$$

$$\begin{aligned}
 Z(T, p) &= U - TS + pV = C_V T + U_0 - T(C_p \log_e T - R \log_e p + S_0) + RT = \\
 &= C_p T(1 - \log_e T) + RT \log_e p - TS_0 + U_0;
 \end{aligned}$$

$$H(S, p) = U + pV = C_V T + U_0 + RT = C_p T + U_0,$$

but $S = C_p \log_e T - R \log_e p + S_0$, whence

$$T = p^{1-\gamma} \exp [(S - S_0) / C_p],$$

and therefore

$$H(S, p) = C_p p^{1-\gamma} \exp [(S - S_0) / C_p] + U_0.$$

74. (a) $dH = TdS + Vdp$, whence it can be seen that, in terms of the independent variables p and H , the entropy $S(p, H)$ is a thermodynamic potential:

$$dS = (1/T)dH - (V/T)dp$$

and

$$T = 1/(\partial S / \partial H)_p, \quad V = -(\partial S / \partial p)_H / (\partial S / \partial H)_p.$$

(b) $dF = -SdT - pdV$, whence it can be seen that, in terms of the independent variables T and F , the volume $V(T, F)$ is a thermodynamic potential:

$$dV = -(S/p)dT - (1/p)dF$$

and

$$p = -1/(\partial V / \partial F)_T, \quad S = (\partial V / \partial T)_F / (\partial V / \partial F)_T.$$

75. $C_p - C_V = T(\partial p / \partial T)_V (\partial V / \partial T)_p$. From $dF = -SdT - pdV$ and $dZ = -SdT + Vdp$ we find

$$(\partial p / \partial T)_V = (\partial S / \partial V)_T, \quad (\partial V / \partial T)_p = -(\partial S / \partial p)_T,$$

and therefore

$$C_p - C_V = -T(\partial S / \partial V)_T (\partial S / \partial p)_T.$$

In order to determine the temperature dependence of the derivatives $(\partial S / \partial V)_T$ and $(\partial S / \partial p)_T$ we shall find the free energy of the crystal at low temperatures. Since $C_V = (\partial U / \partial T)_V = \alpha T^3$, then the temperature dependence of the internal energy is determined by the formula $U = \int \alpha T^3 dT = (\alpha/4)T^4$, and the free energy is equal to

$F = -T \int (U/T^2) dT = -(\alpha/12)T^4$. Therefore $S = -(\partial F/\partial T)_V = (\alpha/3)T^3$, whence $(\partial S/\partial V)_T \sim T^3$ and $(\partial S/\partial p)_T \sim T^3$, and consequently $C_p - C_V \sim T^3$.

76 The internal energy of a plasma is made up of the kinetic energy of random motion of the particles U_{id} (the internal energy of an ideal gas) and the average energy of their electrostatic interaction U_e :

$$U = U_{id} + U_e.$$

The value of U_{id} is known: $U_{id} = C_V T + U_0$. According to a formula of electrostatics, the energy U_e is equal to

$$U_e = (1/2) \sum_{i=1}^{2N} e_i \varphi_i,$$

where φ_i is the potential of the field generated, at the place where the i -th charge is found, by all remaining charges.

In the case of plasma consisting of two kinds of oppositely charged particles we have

$$U_e = (1/2)Ne\varphi_+ - (1/2)Ne\varphi_- = (1/2)Ne(\varphi_+ - \varphi_-),$$

where φ_+ (φ_-) is the potential of the field generated by all the charges, except the given positive (negative) charge, at the place where this charge is found.

Let us find φ_+ and φ_- . In the immediate vicinity of the given charge e there obviously prevail charges of opposite sign. If at a certain distance r from this charge there is a concentration of positive charges equal to n_+ and negative charges n_- , then the charge density at this place will be $\varrho(r) = e(n_+ - n_-)$. The potential of the field generated by all the charges (including the charge e) is determined by Poisson's equation

$$\nabla^2 \varphi(r) = -4\pi \varrho(r).$$

The charged particles are found in this (self-matching) field generated by them. Their concentration n_+ and n_- at a given place is determined by Boltzmann's formula (similarly to the barometric formula for the density of particles in a gravitational field at a height Z : $n(Z) = n_0 \exp(-mgZ/kT)$):

$$n_+(r) = n_0 \exp(-e\varphi/kT) \quad \text{and} \quad n_-(r) = n_0 \exp(e\varphi/kT),$$

where T is the absolute temperature, $k = R/N$ is Boltzmann's constant, $n_0 = N/V$ is the mean concentration of charged particles of one sign. Thus

$$\varrho = en_0 [\exp(-e\varphi/kT) - \exp(e\varphi/kT)]$$

and

$$\nabla^2 \varphi = 4\pi en_0 [\exp(e\varphi/kT) - \exp(-e\varphi/kT)].$$

In the case of a rarefied plasma the mean electrical energy of the charge, $e\varphi$, is small in comparison with the energy of its thermal motion $(3/2)kT$, and therefore

$$\exp(e\varphi/kT) = 1 + (e\varphi/kT) \quad \text{and} \quad \nabla^2 \varphi = \kappa^2 \varphi, \quad \text{where} \quad \kappa^2 = 8\pi e^2 n_0 / kT.$$

Owing to the spherical symmetry of the field $\nabla^2 \varphi = (1/r)d^2(r\varphi)/dr^2$, and therefore $d^2(r\varphi)/dr^2 = \kappa^2(r\varphi)$, whence

$$r\varphi = C_1 \exp(-\kappa r) + C_2 \exp(\kappa r) \quad \text{and} \quad \varphi(r) = (C_1/r) \exp(-\kappa r) + (C_2/r) \exp(\kappa r).$$

The constant $C_2 = 0$, since in the opposite case we would obtain an infinitely large potential far away ($r \rightarrow \infty$) from the given charge, which is meaningless. Thus

$$\varphi(r) = (C_1/r) \exp(-\kappa r).$$

The potential of the field generated by all the charges, except the given charge e , at a point at a distance r from it is evidently equal to

$$\varphi_1(r) = (C_1/r) \exp(-\kappa r) - (e/r),$$

and, at the place where the charge itself is found ($r = 0$), it will be

$$\begin{aligned}\varphi_+ &= \lim_{r \rightarrow 0} (1/r) [C_1 \exp(-\kappa r) - e] = \\ &= \lim_{r \rightarrow 0} (1/r) [C_1 - C_1 \kappa r + (1/2)C_1(\kappa r)^2 - \dots - e] = \\ &= \lim_{r \rightarrow 0} [(C_1 - e)/r] - C_1.\end{aligned}$$

In order that this quantity be finite it is necessary to put $C_1 = e$, and then

$$\begin{aligned}\varphi_+ &= -e\kappa \quad \text{and} \quad \varphi_- = e\kappa, \\ \varphi(r) &= (e/r) \exp(-\kappa r) \quad \text{and} \quad \varphi_1(r) = e[\exp(-\kappa r) - 1]/r.\end{aligned}$$

It can be seen from the formula obtained for $\varphi(r)$ that the potential of the field about a given charge e in a plasma decreases exponentially. In this a plasma differs in principle from a dielectric homogeneous medium in which the field due to an external charge at an arbitrary distance from it decreases by ϵ times in comparison with the free-space field.

The quantity $d = 1/\kappa = (kTV/8\pi e^2 N)^{1/2}$ characterizes the rate of decrease of the potential of the field of a charge in a plasma (i.e. the penetration depth of the external electric field in a plasma) and is called Debye's radius. The more rapid than Coulombian decrease of the potential of the field of a charge in a plasma is due to the presence, about this charge, of a cloud of particles of opposite sign, which leads to weakening, by screening, of the field of the given charge.

Thus

$$U_e = (1/2)Ne(\varphi_+ - \varphi_-) = -Ne^2\kappa = -e^2N/d = -Ne^2(8\pi e^2 N/kTV)^{1/2}$$

and

$$U = C_V T - Ne^2(8\pi e^2 N/kTV)^{1/2}.$$

Whereas the internal energy of an ideal gas U_{id} does not depend on its volume, the energy U_e is inversely proportional to $V^{1/2}$ and for a highly rarefied plasma ($V \rightarrow \infty$) $U_e \rightarrow 0$ as a consequence of the tending to zero of the interaction between particles.

77. (a) $F = U - TS$,

$$\begin{aligned}\Delta F &= \Delta U - \Delta(TS) = \\ &= C_V(T_2 - T_1) - [T_2(C_V \log_e T_2 + R \log_e V_2 + S_0) - T_1(R \log_e V_1 + C_V \log_e T_1 + S_0)] = \\ &= C_V(T_2 - T_1) - R(T_2 \log_e V_2 - T_1 \log_e V_1) - C_V(T_2 \log_e T_2 - T_1 \log_e T_1) - (T_2 - T_1)S_0.\end{aligned}$$

For $V_1 = V_2 = 1l$ for a diatomic ideal gas ($C_V = 5$ cal/degree-mole) we have

$$\Delta F = 5 \times 100 - 5(373 \log_e 373 - 273 \log_e 273) - 100 S_0 = (-2885.7 - 100 S_0) \text{ cal/mole.}$$

$$Z = F + pV,$$

$$\begin{aligned}\Delta Z &= \Delta F + \Delta(pV) = \Delta F + V(p_2 - p_1) = \\ &= -2885.7 - 100 S_0 + 1[(373/273) - 1] 22.4 \times 24.214 = -2687 - 100 S_0 \text{ cal/mole.}\end{aligned}$$

$$(b) \Delta F = C_p(T_2 - T_1) - R(T_2 \log_e p_2 - T_1 \log_e p_1) - C_p(T_2 \log_e T_2 - T_1 \log_e T_1) - (T_2 - T_1)S_0.$$

For $p_1 = p_2 = 1$ atm:

$$\Delta F = 7 \times 100 - 7(373 \log_e 373 - 273 \log_e 273) - 100 S_0 \approx (-4000 - 100 S_0) \text{ cal/mole,}$$

$$\begin{aligned}\Delta Z &= \Delta F + p(V_2 - V_1) = -4000 - 100 S_0 - [(373/273) - 1] 22.4 \times 24.214 = \\ &= (-3800 - 100 S_0) \text{ cal/mole.}\end{aligned}$$

78. According to the Gibbs-Helmholtz equation

$$\mathcal{C} = (Q_p/zF) + T(\partial \mathcal{C} / \partial T)_p,$$

where Q_p is the heat of reaction referred to one mole, and Q_p/zF is the heat of reaction referred to a unit charge (z is the valency and F is Faraday's number).

For $t = 25^\circ\text{C}$ the e. m. f. of the cell is equal to

$$\mathcal{E} = 0.96466 V,$$

whereby the following is supplied at the expense of the heat reservoir

$$T(\partial\mathcal{E}/\partial T)_p = 298 \times 1.74 \times 10^{-4} = 4.585 \times 10^{-2} V.$$

The heat of reaction referred to one Coulomb of charge flowing through the cell is equal to $Q_p z F = \mathcal{E} - T(\partial\mathcal{E}/\partial T)_p = 0.96466 - 4.585 \times 10^{-2} = 0.9188$ Joule/Coulomb = 0.1905 cal/Coulomb.

79. Let us assume that a chemical reaction that takes place for the flowing of current through the cell is accompanied by volume variation. Let the free energy and volume have initial values F_1 and V_1 and be equal to F_2 and V_2 after the flowing of a unit charge. The external pressure p and the temperature T are constant. The decrease of free energy is equal to the work spent for the displacement of a unit charge and for the increase of volume: \mathcal{E} and $p(V_2 - V_1)$ respectively. Thus

$$F_1 - F_2 = \mathcal{E} + p(V_2 - V_1),$$

whence

$$(\partial F_1/\partial p)_T - (\partial F_2/\partial p)_T = (\partial\mathcal{E}/\partial p)_T + p[(\partial V_2/\partial p) - (\partial V_1/\partial p)]_T + V_2 - V_1.$$

However, from $dF = -SdT - pdV$ we have

$$(\partial F/\partial p)_T = -p(\partial V/\partial p)_T,$$

and therefore

$$(\partial\mathcal{E}/\partial p)_T = V_1 - V_2.$$

This formula shows that if the chemical reaction in the cell is accompanied by volume increase ($V_2 > V_1$), then the e. m. f. decreases for an increase of external pressure and vice versa. If the reaction takes place between liquid or solid bodies, then the volume variation is negligible and in this case the e. m. f. is practically independent of pressure; in gas cells, however, the pressure dependence of the e. m. f. is very important.

80. The isenthalpicity of the Joule-Thomson process is established by using the first law only, which is always expressed (both in reversible and irreversible processes) in the form of an equality and which, therefore, does not enable us to account for irreversibility. The derivatives $(\partial H/\partial p)_T$ and $(\partial H/\partial T)_p$ for determining μ are found from the fundamental equation of thermodynamics (and therefore from the first law) for equilibrium processes. Thus, in the evaluation itself of μ , according to (5.7), the irreversibility of the Joule-Thomson process is not taken into account. This, however, does not affect the result, since enthalpy, just as any other thermodynamic potential, is a single-valued parameter of state and its variation does not depend on the character of the process but is only determined by the initial and final states of the system.

81. In the case of a van der Waals' gas we obtain, from (5.7), for the inversion temperature the equation

$$(2a/V^2) - RTb/(V - b)^2 = 0.$$

If we determine V from here and substitute it in van der Waals' equation, then we shall find T_i as a function of the pressure p

$$T_i = (8/9Rb) [1 \pm (1/2)(1 - 3b^2a^{-1}p)^{1/2}]^2.$$

It can be seen from this formula that for large densities there exist two points of inversion. The coefficient μ is positive above the upper inversion point and below the lower inversion point. Between these points it is negative. The position of these points depends on pressure: with a pressure increase the upper point lowers and the lower one

risers. This is qualitatively in accordance with experiment. The lower inversion point lies in the liquid state and is observed in many substances.

82. Even if, in contradiction to the theory of relativity, we add up the velocity of light as is shown in the text, then there is still an error in the reasoning, that has

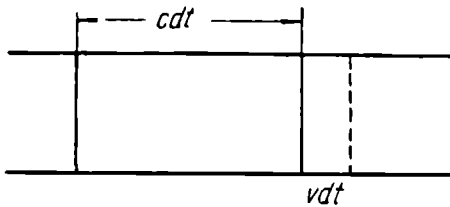


FIG. 57.

escaped attention. It consists in that it has been incorrectly assumed that the energy difference $\delta Q - \delta Q_1 = uvdt$ goes into work for the displacement of the body. In fact, as can be seen from Fig. 57, this energy does not go into work of displacement of the body for its motion under the action of light pressure, but is found in a space of volume vdt and has no relation whatsoever to the work of the force of light pressure. The displacement of the body with velocity v can only be caused by external forces and in this connexion v can have an arbitrary value, but this does not affect at all the calculation given in the text. Notwithstanding this, a correct result is obtained for radiation pressure as a consequence of the arbitrariness of equating the work of the force of pressure pdx to the value of the radiation energy $uvdt$, which does not enter, during the time dt , the body owing to its motion.

83. The functions U , F , Z and H are potentials if they are expressed respectively in terms of the variables:

$$U = U(S, V), \quad F = F(T, V), \quad Z = Z(T, p) \quad \text{and} \quad H = H(S, p).$$

For equilibrium radiation $U = uV$, where the energy density u , by the Stefan-Boltzmann law, is equal to σT^4 , since $U = \sigma T^4 V$. However, this expression for U is not a potential. We have to express T in terms of S and V . From the expression for the entropy of radiation $S = (4/3)\sigma T^3 V$ we find

$$T = (3S/4\sigma V)^{1/3}$$

and

$$U = \sigma V(3S/4\sigma V)^{4/3}.$$

The free energy is

$$F = U - TS = \sigma T^4 V - T(4/3)\sigma T^3 V = -(1/3)\sigma T^4 V.$$

Gibbs' thermodynamic potential is

$$Z = F + pV = -(1/3)\sigma T^4 V + (1/3)\sigma T^4 V = 0.$$

The enthalpy is

$$H = U + pV = (4/3)\sigma T^4 V = TS = S(3p/\sigma)^{1/4}.$$

It can be seen from this that the thermodynamic potential $Z(t, p)$ for equilibrium radiation cannot serve as a characteristic function; this is caused by the fact that p and T for radiation are not independent variables ($p = (1/3)\sigma T^4$).

84. Let us assume the contrary: let us assume that, after a quasi-static adiabatic expansion from density u_1 to density u_2 , radiation has ceased to be black in its spectral composition. Since black-body radiation is a system that is found in stable equilibrium (see problem no. 93), we must expect that if the radiation u_2 is put in contact with a body of temperature T_2 with which it will be found in equilibrium (i.e. the total quantity of radiation energy does not vary), then the radiation will become black in the course of time. The system passes without variation of its total energy to stable equilibrium, which is connected with an increase of entropy. Therefore the entropy of black radiation of density u_2 must be larger than the entropy of black radiation of the initial state with density u_1 .

Let us consider now the inverse process of adiabatic compression to reach the initial density u_1 . The radiation entropy does not vary in this connexion, but, according to our assumption, the radiation has a different spectral composition from black radiation at the initial temperature T_1 . At the same time its entropy is larger than the entropy of black radiation with the same energy. By contact with a body T_1 this radiation becomes black, corresponding to stable equilibrium, but this process of transition to stable equilibrium must be connected with a decrease of entropy without any compensation in surrounding bodies—which contradicts the second law.

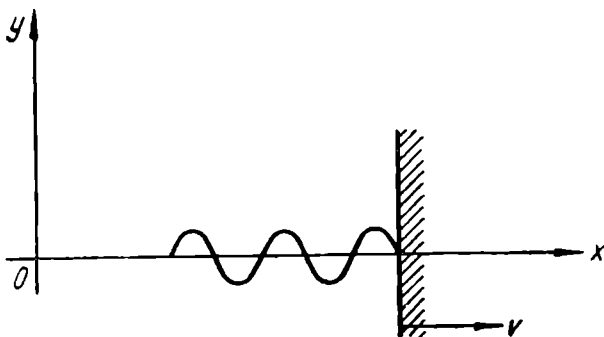


FIG. 58.

Thus the adiabatic process with black radiation converts it to black radiation, again, of a different temperature.

85. The variations undergone by black radiation in an adiabatic expansion can only be caused by the moving piston which is a white mirror. In the reflection of light from a moving mirror both the frequency and intensity of light vary. In addition the angle of reflection is not equal to the angle of incidence.

The frequency variation can be found from the Doppler principle, but also more simply by proceeding as follows. Let light be propagated along the x axis (Fig. 58).

Then we can write for the incident ray

$$E_y = a \cos 2\pi \nu(t + xc^{-1}),$$

and for the reflected ray

$$E'_y = a' \cos 2\pi \nu'(t - xc^{-1}).$$

On the mirror surface, i.e. on the $x = vt$ surface, the connexion between E_y and E'_y does not vary with time and therefore the coefficients qualifying t under the sign of cosine are left unvaried in both expressions for $x = vt$. Hence

$$\nu'(1 + vc^{-1}) = \nu(1 - vc^{-1})$$

or, by neglecting higher powers of vc^{-1} ,

$$\nu' = \nu(1 - 2vc^{-1})$$

and

$$d\nu' = d\nu(1 - 2vc^{-1}).$$

Here v is the velocity of the mirror in the ray direction, i.e. along the x axis.

If a ray is propagated at an angle α to the x axis (or to the normal to the mirror as is shown in Fig. 59), then for the motion of the mirror

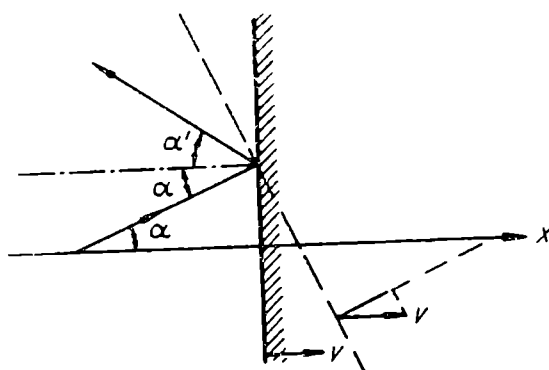


FIG. 59.

with velocity v with respect to the x axis, along the ray its velocity will be $v \cos \alpha$ and then we have

$$\nu' = \nu(1 - 2vc^{-1} \cos \alpha)$$

and

$$d\nu' = d\nu(1 - 2vc^{-1} \cos \alpha).$$

Since for each ray $E = h\nu$, then for a variation of the frequency ν and of the interval $d\nu$, the energy of the portion of radiation (with frequencies within ν , $\nu + d\nu$) will vary by as many times

$$U' = U(1 - 2\nu c^{-1} \cos \alpha) \\ (U = uV = U_\nu d\nu = u_\nu V d\nu).$$

It is evident that all these variations are connected with each other by the relations

$$\nu'/\nu = d\nu'/d\nu = U'/U.$$

It suffices therefore to determine one of these variations in order to evaluate also the others.

The energy variation of monochromatic radiation with frequencies between ν and $\nu + d\nu$ for the motion of the piston can be found by evaluating the work of light pressure on the piston. Let the light pressure on the moving piston be equal to c' . By assuming $\nu \ll c$, we can take $p' = p$, i.e. equal to the pressure on the still piston.

For a volume variation of the cavity by dV the work of the selected portion of radiation is equal to

$$pdV = (u/3)dV = (U/3V)dV.$$

This work is equal to the energy decrease dU . Thus

$$-dU = (U/3V)dV,$$

whence

$$-dU/U = (1/3)dV/V \quad \text{and} \quad U'/U = V^{1/3}/V'^{1/3}.$$

Since in an adiabatic process $VT^3 = V'T'^3$, then from

$$\nu'/\nu = d\nu'/d\nu = U'/U = V^{1/3}/V'^{1/3} = T'/T$$

we find

$$\nu/T = \nu'/T' = \text{const}$$

and

$$T'/T = U'/U = u_\nu V' d\nu'/u_\nu V d\nu = (u_\nu'/u_\nu) (T^3/T'^3) (T'/T)$$

or

$$u_\nu/T^3 = u_\nu'/T'^3 = \text{const}.$$

86. We have for equilibrium radiation

$$U = \sigma T^4 V \quad \text{and} \quad p = \sigma T^4/3,$$

and therefore $C_V = 4\sigma T^3 V$ and the specific thermal capacity at constant volume is

$$c_V = 4\sigma T^3 = 7.3 \times 10^{-22} T^3 \text{ cal/degree} \times \text{cm}^3.$$

Since an isobaric process for radiation is at the same time isothermal, then

$$C_p = C_T = \infty,$$

since the isothermal capacity is equal to infinity. Therefore

$$\gamma = C_p/C_V = \infty,$$

$$C_p - C_V = \infty$$

and

$$pV^\gamma = \infty.$$

The energy of a mole of monatomic gas is

$$U = (3/2) RT,$$

the molecular thermal capacity is

$$C_V = (3/2) R,$$

and the specific thermal capacity is

$$c_V = 3R/2V = 3 \times 2/(2 \times 22.4 \times 10^3) = 1.3 \times 10^{-4} \text{ cal/degree} \times \text{cm}^3.$$

Thus

$$(c_V)_{\text{rad}}/(c_V)_{\text{gas}} = 5.6 \times 10^{-8} T^3$$

which is an extremely small quantity at ordinary temperatures ($\sim 300^\circ\text{K}$). The two quantities become comparable at $T \approx (10^8)^\circ\text{K}$.

87. A thermodynamic analysis of radiation leads to the fact that, when a ray is resolved into a reflected and a refracted ray, the sum of the entropies of these rays is larger than the entropy of the incident ray. From the entropy increase in the splitting of a ray, itself a correct result, the incorrect result has been derived that the process of decomposition of light is irreversible. This result has also been justified by proceeding from other methods.

(a) Since for a constant ν the energy spectral density $u_\nu(\nu, T)$ can only decrease owing to temperature decrease of the beam, then it can be said that the initial beam of rays of temperature T is split into two beams of lower temperature (since the energy density in them is smaller): in splitting, radiation temperature decreases. This is, however, an irreversible process, since the reverse process would be impossible without compensation. We can rebut this argument in the following manner: this phenomenon can be completely reversed by letting the reflected and transmitted rays travel in the reverse direction by means of two mirrors set perpendicularly to these rays. The latter then again combine into an incident beam (travelling now in the opposite direction), and the process has been completely reversed without any variations in the surrounding bodies. Thus we must state, on the contrary, that the process of regular reflection and refraction is completely reversible. The contradiction arising has been incorrectly resolved by trying to justify the irreversibility of the process of decomposition of light. This has been done in the following manner (Fig. 60).

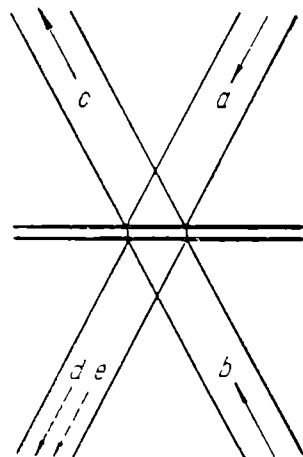


FIG. 60.

(b) In reversing the decomposition of a ray (travelling to the surface in the reverse direction to the ray c and splitting into rays opposite to the rays a and b) the ray a and the ray b should have acted together in such a manner as to give a single light ray c . However, from the single ray a there would arise the ray d and also from the single ray b there would arise the reflected ray e . Thus the rays a and b combine to give a single ray c , only in the case when we can make the rays d and e annul each other. This is theoretically possible if they have equal amplitudes and rigorously opposite phases. To achieve this would require such high accuracy that the impossibility of such an experiment can be stated, as well as the impossibility of achieving the reversibility of the expansion of a single ray. Both above arguments are incorrect: the correct solution of the problem is given in § 26.

$$\begin{aligned} 88. Z &= U - TS + pV = C_V T - T(C_p \log_e T - R \log_e p + S_0) + RT = \\ &= RT \log_e p - C_p T(1 - \log_e T) + TS_0, \end{aligned}$$

$$\mu = (\partial Z / \partial N)_{T, p} = kT \log_e p - c_p T(1 - \log_e T) + Ts_0 = kT \log_e p + \mu_0(T).$$

For equilibrium radiation $Z = U - TS + pV = \sigma T^4 V - T(4/3)\sigma T^3 V + (1/3)\sigma T^4 V = 0$ and therefore $\mu = 0$.

89. The fundamental equation for a system with a variable number of particles has the form

$$TdS = dU + pdV - \sum_i \mu_i dN_i.$$

By means of Legendre's transformation this equation can be written in the form

$$-SdT = d(U - TS - \sum_i \mu_i N_i) + pdV + \sum_i N_i d\mu_i$$

or

$$d\omega = -SdT - pdV - \sum_i N_i d\mu_i,$$

where

$$\omega = U - TS - \sum_i \mu_i N_i = U - TS - Z = -pV.$$

It can be seen from this that the thermodynamic potential in terms of the independent variables T , V , μ_i is the function $\omega(T, V, \mu) = -pV$

$$\begin{aligned} S &= -(\partial\omega/\partial T)_{V, \mu}, \\ p &= -(\partial\omega/\partial V)_{T, \mu}, \\ N_i &= -(\partial\omega/\partial\mu_i)_{T, V}. \end{aligned}$$

90. If p and T are assigned and are the same in both phases, while $\mu_1(p, T)$ and $\mu_2(T, p)$ are the chemical potentials of these phases, N_1 and N_2 are the number of particles in each phase, then the thermodynamic potential of a two-phase system will be

$$Z = N_1\mu_1(T, p) + N_2\mu_2(T, p),$$

whereby

$$N_1 + N_2 = \text{const.}$$

The internal parameters are N_1 and N_2 and thus $\delta N_1 + \delta N_2 = 0$, then $\delta N_2 = -\delta N_1$. From the equilibrium condition $\delta Z = 0$ we have

$$\delta Z = (\mu_1 - \mu_2)\delta N_1 = 0,$$

which reduces to the equality

$$\mu_1(p, T) = \mu_2(T, p)$$

i.e. in the presence of equilibrium of the phases the chemical potentials must be equal.

91. Let us take the gas volume V as the parameter. We have for an ideal gas

$$dS = (C_V/T)dT + (R/V)dV.$$

From $\delta Q = C_V dT + p_0 dV$ in the presence of adiabatic insulation ($\delta Q = 0$) we have $C_V dT = -p_0 dV$ and therefore

$$dS = (1/T)(RTV^{-1} - p_0)dV = (1/T)(p - p_0)dV,$$

where $p = RT/V$ is the gas pressure. It can be seen from this that equilibrium ($dS = 0$) is only possible for $p = p_0$ by which, as we shall now show, the entropy is in this case a maximum. The entropy of an ideal gas is equal to

$$S = C_V \log_e T + R \log_e V + S_0.$$

Let the gas volume be varied by δV and the temperature by δT . Then

$$\begin{aligned} \Delta S &= C_V \log_e [(T + \delta T)/T] + R \log_e [(V + \delta V)/V] \approx \\ &\approx C_V \delta T/T + R \delta V/V - (1/2)(C_V T^{-2} \delta T^2 + R V^{-2} \delta V^2) = \\ &= T^{-1}(RTV^{-1} - p_0)\delta V - (1/2)(C_V T^{-2} \delta T^2 + R V^{-2} \delta V^2), \end{aligned}$$

whence

$$\delta S = T^{-1}(p - p_0)\delta V, \\ \delta^2 S = -(C_V T^{-2}\delta T^2 + R V^{-2}\delta V^2).$$

It can be seen from the expression for $\delta^2 S$ that it is always negative for arbitrary values of δT and δV . Therefore entropy is a maximum at equilibrium.

92. The basic equation of thermodynamics for non-static processes (6.4), expressed in terms of the independent variables S and p , takes the form

$$dH < TdS + Vdp,$$

whence it can be seen that in a system with $S = \text{const}$ and $p = \text{const}$, equilibrium occurs for a minimum of enthalpy.

From the fundamental equation (6.4)

$$dU < TdS - pdV$$

we also see that in a system with constant entropy and volume, equilibrium occurs for a minimum of internal energy.

93. Radiation emitted from different bodies into a cavity with white walls is found in thermodynamic equilibrium although the temperatures of the various rays are different. This equilibrium is not stable since it possesses no entropy maximum. However, if a speck of dust is introduced in the cavity, then we obtain equilibrium radiation corresponding, as we shall show, to stable equilibrium with one and the same temperature for all rays.

Stable equilibrium between rays of different frequencies occurs for a maximum of entropy

$$s = \int_0^\infty s(\nu) d\nu, \quad (1)$$

if the energy (or energy density) $u = \int_0^\infty u(\nu) d\nu$ remains constant. This means that

for a possible small transition of energy from one frequency to another the variation of entropy is $\delta s = 0$ for $\delta u = 0$, i.e.

$$\delta s = \int_0^\infty \delta s(\nu) d\nu = \int_0^\infty [\partial s(\nu)/\partial u(\nu)] \delta u(\nu) d\nu = 0$$

for

$$\delta u = \int_0^\infty \delta u(\nu) d\nu = 0.$$

These conditions must be verified for arbitrary possible values of δu , however we may choose the latter. A sufficient and necessary expression for this is the condition that the quantity $\partial s(\nu)/\partial u(\nu)$ shall have one and the same value for all frequencies, i.e.

$$\partial s(\nu)/\partial u(\nu) = C.$$

The quantity C has for each black radiation a determined value, one and the same for all frequencies. It follows from this that it can be a function only of temperature and, as we shall now show, it is equal to $1/T$. In fact, suppose that, in communicating to a cavity of volume $V = 1 = \text{const}$ a certain quantity of heat, the radiation temperature has become $T + dT$. Then the entropy s has varied by the amount $(ds/dT)dT = (T^{-1})(du/dT)dT$, since $Tds = du$ (for $V = \text{const}$). But from (1)

$$ds/dT = \int_0^\infty [\partial s(\nu)/\partial u(\nu)] \cdot [\partial u(\nu)/\partial T] d\nu = C \int_0^\infty [\partial u(\nu)/\partial T] d\nu,$$

i.e.

$$ds/dT = Cdu/dT$$

and therefore $C = 1/T$.

Thus equilibrium radiation (which is established in the cavity after a speck of dust has been introduced into it) is a system of rays in stable equilibrium at one and the same temperature—the temperature of the speck of dust or of the walls.

94. By the definition of thermodynamic equilibrium, the temperature in all parts of a body will be one and the same. Let us find the second equilibrium condition for a body that is found in a field in which the potential energy referred to one particle is equal to φ , by proceeding from the minimum of Gibbs' thermodynamic potential at equilibrium.

The various parts of the body are found under different conditions in the presence of a field. The energy variation of a small part of the body is determined not only, as before (in the absence of field), by the quantity $dU = TdS - pdV + \mu dN$ but also by the variation of the potential energy of the particles occurring in the part of the body considered. We have, therefore, for a system in a field

$$dU = TdS - pdV + \mu dN + \varphi dN,$$

whence

$$\begin{aligned} dZ &= -SdT + Vdp + (\mu + \varphi)dN, \\ \mu + \varphi &= (\partial Z / \partial N)_{T, p}, \end{aligned}$$

and Gibbs' thermodynamical potential of the whole body is

$$Z = \int (\mu + \varphi) dN.$$

The equilibrium condition with respect to the distribution of the particles will be

$$\delta Z = \int (\mu + \varphi) \delta(dN) = 0$$

when the total number of particles in the body is retained

$$\int \delta(dN) = 0.$$

We obtain from this that for the equilibrium of a body in a field the following condition must be observed

$$\mu + \varphi = \text{const},$$

i.e. the "complete" potentials of all parts of the body must be equal to each other.

In the gravitational field φ is a function of the coordinates x , y and z of the centre of gravity of the molecules, and we have, therefore, at equilibrium

$$\mu(T, p) + \varphi(x, y, z) = \text{const}. \quad (1)$$

It can be seen from this that under equilibrium conditions of the system the pressure is different in different parts; in the absence of a field p is everywhere the same. By differentiating (1) we shall obtain

$$d\mu + d\varphi = 0.$$

In the case of a homogeneous gravitational field when $\varphi = mgz$, we have

$$vdp + mgz = 0$$

and, since $m/v = \varrho$ is the density of the medium we obtain

$$dp = -\varrho g dz,$$

i.e. the known expression for the height variation of the hydrostatic pressure of gas or liquid.

95. For a system in its entirety the stability conditions (6.27) are valid in the case of a homogeneous medium when pressure is the same at all points, while the thermal capacity of the entire system is equal to the sum of the thermal capacities of its parts. For an inhomogeneous system these conditions are true only locally and cannot be applied to the system as a whole. In the presence of a field, for example, the pressure is different at different places, and the energy, and, hence, the thermal capacity are

non-additive. Therefore from the fact that $C_V > 0$ for a small part of a star it does not follow that the thermal capacity will be positive for the star as a whole.

96. Let us take as the internal parameters the entropy and volume of the system. From the general condition of equilibrium of a system in a thermostat with constant pressure ($\Delta Z > 0$) for virtual [variations] of S and V , we find

$$\Delta Z = \Delta U - T_0 \delta S + p_0 \delta V > 0,$$

where S , U and V are parameters of the system while T_0 and p_0 are the constant values of the temperature and pressure of the thermostat.

The variation ΔU for virtual variations of S and V is equal to

$$\begin{aligned} \Delta U &= (\partial U / \partial S)_V \delta S + (\partial U / \partial V)_S \delta V + (1/2)[(\partial^2 U / \partial S^2) \delta S^2 + 2(\partial^2 U / \partial S \partial V) \delta S \delta V + \\ &\quad + (\partial^2 U / \partial V^2) \delta V^2] = \\ &= T \delta S - p \delta V + (1/2)[(\partial^2 U / \partial S^2) \delta S^2 + 2(\partial^2 U / \partial S \partial V) \delta S \delta V + (\partial^2 U / \partial V^2) \delta V^2], \end{aligned}$$

neglecting terms of the third order with respect to variations δS and δV , and also using the fact that $(\partial U / \partial S)_V = T$ and $(\partial U / \partial V)_S = -p$.

Thus the condition (6.16) assumes the form

$$\Delta Z = (T - T_0) \delta S + (p_0 - p) \delta V + (1/2)[(\partial^2 U / \partial S^2) \delta S^2 + (\partial^2 U / \partial S \partial V) \delta S \delta V + (\partial^2 U / \partial V^2) \delta V^2] > 0,$$

whence

$$\delta Z = (T - T_0) \delta S + (p_0 - p) \delta V$$

and

$$\delta^2 Z = (\partial^2 U / \partial S^2) \delta S^2 + 2(\partial^2 U / \partial S \partial V) \delta S \delta V + (\partial^2 U / \partial V^2) \delta V^2.$$

From $\delta Z = 0$ we find $T = T_0$ and $p = p_0$, i.e. under equilibrium conditions the systems temperature and pressure are found to be equal to the thermostat temperature and pressure respectively.

The condition for equilibrium stability of our system will be $\delta^2 Z > 0$ or

$$(\partial^2 U / \partial S^2) \delta S^2 + 2(\partial^2 U / \partial S \partial V) \delta S \delta V + (\partial^2 U / \partial V^2) \delta V^2 > 0. \quad (2)$$

This expression is a quadratic function of the variations δS and δV . It is known from algebra that an expression of the type $ax^2 + 2bxy + cy^2$ is always positive if $a > 0$ and $ac - b^2 > 0$. Therefore we have the following conditions for equilibrium stability of a homogeneous system

$$(\partial^2 U / \partial S^2) > 0 \quad (3)$$

and

$$(\partial^2 U / \partial S^2) \cdot (\partial^2 U / \partial V^2) - (\partial^2 U / \partial S \partial V)^2 > 0. \quad (4)$$

The first of these conditions means that

$$(\partial^2 U / \partial S^2) = (\partial T / \partial S)_V = T / C_V > 0,$$

i.e.

$$C_V > 0, \quad (5)$$

since we have taken $T > 0$.

The second condition can be expressed in the form of a Jacobian and it gives

$$\begin{aligned} (\partial^2 U / \partial S^2) \cdot (\partial^2 U / \partial V^2) - (\partial^2 U / \partial S \partial V)^2 &= \begin{vmatrix} \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial S} \right) & \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial S} \right) \\ \frac{\partial}{\partial S} \left(\frac{\partial U}{\partial V} \right) & \frac{\partial}{\partial V} \left(\frac{\partial U}{\partial V} \right) \end{vmatrix} = \\ &= \partial \left(\frac{\partial U}{\partial S}, \frac{\partial U}{\partial V} \right) / \partial(S, V) = \partial(T, -p) / \partial(S, V) = -\partial(T, p) / \partial(S, V) > 0 \end{aligned}$$

i.e.

$$\partial(T, p) / \partial(S, V) < 0.$$

By using the property of Jacobians this inequality can be easily transformed to

$$\begin{aligned}\partial(T, p)/\partial(S, V) &= [\partial(T, p)/\partial(T, V)] \cdot [\partial(T, V)/\partial(S, V)] = \\ &= (\partial p/\partial V)_T (\partial T/\partial S)_V = (T/C_V) (\partial p/\partial V)_T < 0,\end{aligned}$$

whence

$$(\partial p/\partial V)_T < 0, \quad (6)$$

since, according to (5), $C_V > 0$.

Thus the conditions for equilibrium stability of a physically homogeneous system are

$$C_V > 0 \quad \text{and} \quad \varepsilon_T = -V_0(\partial p/\partial V)_T > 0, \quad (7)$$

i.e. the thermal capacity at constant volume and the isothermal modulus of elasticity must be positive for equilibrium of the system. However, since, according to (3.54), $C_p - C_V > 0$, it follows that at equilibrium $C_p > 0$.

The condition $T/C_V > 0$ will be satisfied for $T = 0$, if the temperature dependence of C_V for $T \rightarrow 0$ has the form $C_V = aT + bT^2 + \dots$ ($a > 0$), and therefore C_V must tend to zero for $T \rightarrow 0$. This result cannot, however, be derived unambiguously from the stability condition, since the possibility is not excluded that for $T = 0$ the inequality $T/C_V > 0$ degenerates to the equality $T/C_V = 0$, which would occur, for $T \rightarrow 0$, if the thermal capacity $C_V(0) = \text{const} \neq 0$ or else if it varied according to the law $C_V = aT^n$, where $n < 1$. This ambiguity is resolved in favour of the first alternative, only by Nernst's theorem, which is not a consequence of the first and second laws (see Chapter IX).

97. The work per unit volume of an isotropic magnetic substance, accomplished for a variation of the magnetic field in it, is equal to

$$\delta W = -(1/4\pi)(H, dB) = -(1/4\pi)HdB.$$

The formula (B) is obtained from (A) as a result of replacing B by $H + 4\pi M$

$$\begin{aligned}\delta W &= -(1/4\pi)(H, dB) = (-1/4\pi)(H, dH + 4\pi dM) = \\ &= -d(H^2/8\pi) - (H, dM).\end{aligned}$$

Since for paramagnetic and ferromagnetic substances $H \uparrow \uparrow M$ then

$$(H, dM) = HdM, \quad \delta W = -d(H^2/8\pi) - HdM$$

and

$$dU' = TdS - pdV + HdM.$$

However, for diamagnetic substances $M \uparrow \downarrow H$, and therefore $(H, dM) = -HdM$,

$$\delta W = -d(H^2/8\pi) + HdM$$

and

$$dU' = TdS - pdV - HdM.$$

Therefore the stability condition for diamagnetic substances has the form

$$(\partial H/\partial M)_{S, V} = 1/\kappa < 0,$$

which leads to $\kappa < 0$, in agreement with experiment.

This clarifies the question set in the problem. Thus there is no ground for doubting the correctness of using for magnetic substances the quantity M instead of B .

98. The Le Chatelier-Braun principle establishes the general property of all equilibrium systems to pass under an external disturbance to such a state for which this disturbance is weakened. Let us prove it for systems in which the chemical composition and mass are retained during the processes they undergo (for processes with variation of the mass of the components and phases of the system the Le Chatelier-Braun principle is also valid, but it is proved otherwise).

Let us consider a system the state of which is determined by the variables x_1 and x_2 , and by X_1 and X_2 , the generalized forces associated with them. Let the differential of a certain parameter of state Y be equal to

$$dY = X_1 dx_1 + X_2 dx_2.$$

Then

$$(\partial X_1 / \partial x_2)_{x_1} = (\partial X_2 / \partial x_1)_{x_2} \quad (1)$$

and

$$(\partial x_1 / \partial X_2)_{X_1} = (\partial x_2 / \partial X_1)_{X_2}, \quad (2)$$

since

$$d(Y - X_1 x_1 - X_2 x_2) = -x_1 dX_1 - x_2 dX_2.$$

Let us express the derivative $(\partial x_1 / \partial X_1)_{x_2}$ in terms of the derivatives $(\partial x_1 / \partial X_1)_{X_2}$, $(\partial x_1 / \partial X_2)_{X_1}$ and $(\partial x_2 / \partial X_2)_{X_1}$. By using the properties of Jacobians this can be done in the following manner

$$\begin{aligned} (\partial x_1 / \partial X_1)_{x_2} &= \partial(x_1, x_2) / \partial(X_1, x_2) = [\partial(x_1, x_2) / \partial(X_1, X_2)] \times \\ &\times [\partial(X_1, X_2) / \partial(X_1, x_2)] = [\partial(x_1, x_2) / \partial(X_1, X_2)] (\partial X_2 / \partial x_2)_{X_1}. \end{aligned}$$

But according to (2)

$$\begin{aligned} \frac{\partial(x_1, x_2)}{\partial(X_1, X_2)} &= \begin{vmatrix} \left(\frac{\partial x_1}{\partial X_1}\right)_{X_2} & \left(\frac{\partial x_1}{\partial X_2}\right)_{X_1} \\ \left(\frac{\partial x_2}{\partial X_1}\right)_{X_2} & \left(\frac{\partial x_2}{\partial X_2}\right)_{X_1} \end{vmatrix} = (\partial x_1 / \partial X_1)_{X_2} (\partial x_2 / \partial X_2)_{X_1} - (\partial x_1 / \partial X_2)_{X_1} (\partial x_2 / \partial X_1)_{X_2} \\ &= (\partial x_1 / \partial X_1)_{X_2} (\partial x_2 / \partial X_2)_{X_1} - (\partial x_1 / \partial X_2)_{X_1}^2, \end{aligned}$$

and therefore

$$(\partial x_1 / \partial X_1)_{x_2} = (\partial x_1 / \partial X_1)_{X_2} - (\partial x_1 / \partial X_2)_{X_1}^2 (\partial X_2 / \partial x_2)_{X_1}. \quad (3)$$

Owing to the stability condition (6.27')

$$(\partial x_2 / \partial X_2)_{X_1} > 0, \quad (4)$$

and therefore (3) gives

$$(\partial x_1 / \partial X_1)_{x_2} < (\partial x_1 / \partial X_1)_{X_2}. \quad (5)$$

This inequality is simply the expression of the Le Chatelier-Braun principle. If, in a system in which the parameters x_1 and x_2 are maintained constant, we begin to vary the parameter x_1 by an external disturbance X_1 , then this will give rise to a variation of x_2 and X_2 and a measure of the disturbance will be the quantity $(\partial x_1 / \partial X_1)$. However, for a sudden increase of X_1 , the process can be considered at first as occurring with constant X_2 , and therefore for this time the applied disturbance is characterized by the derivative $(\partial x_1 / \partial X_1)_{X_2}$. When, however, equilibrium is re-established and the parameter x_2 will assume its previous value maintained by the external medium, then the variation of the value of x_1 owing to the external disturbance will be determined by the derivative $(\partial x_1 / \partial X_1)_{x_2}$. The Chatelier-Braun principle states that in the new equilibrium state to which the system has passed the variation of the parameter x_1 owing to the external disturbance has been reduced, i.e.

$$(\partial x_1 / \partial X_1)_{x_2} < (\partial x_1 / \partial X_1)_{X_2}.$$

We can adduce a number of examples in which this principle is manifest.

(1) Let us consider a system in a thermostat. Let us vary at a certain instant the pressure on the system. This will cause a variation of volume and temperature. A measure of the disturbance will be $(\partial V / \partial p)$. At the initial instant, owing to the suddenness of the variation of p , the process is practically adiabatic and therefore the external disturbance is determined by the derivative $(\partial V / \partial p)_S$. After equilibrium has been established and the previous temperature has been restored, the value of the distur-

bance will be determined by the derivative $(\partial V/\partial p)_T$. By the Le Chatelier-Braun principle, in the new equilibrium state the result of the disturbance has been reduced and

$$(\partial V/\partial p)_T < (\partial V/\partial p)_S.$$

This result can easily be obtained directly by using the stability condition $C_p > 0$. In fact from $-dF = pdV + SdT$ it can be seen that in the case given $X_1 = p$, $x_1 = V$, $X_2 = S$, $x_2 = T$, and therefore, according to the condition $C_p > 0$, $(\partial x_2/\partial X_2)_{X_1} = (\partial T/\partial S)_p = T/C_p > 0$, and therefore according to (5), $(\partial V/\partial p)_T < (\partial V/\partial p)_S$.

(2) We may increase the external pressure on a body by decreasing its volume. There arises in this connexion a variation of temperature which is directed in such a manner that it tends to increase the volume again; those bodies therefore that are compressed by heating (for example, water at $t < 4^\circ\text{C}$.) will cool by compression.

(3) If we communicate to a mixture of ice and water a certain quantity of heat, then ice will begin to melt which will eliminate the temperature increase that would otherwise occur.

(4) Let there be two substances in a state of chemical equilibrium. If heat is communicated to them, a reaction will occur which will try to cool the system. Therefore a temperature increase will cause the dissociation of substances formed by exothermal reaction and, on the contrary, endothermal compounds will be formed.

(5) For a salt that is found in a saturated solution a temperature increase will cause its dissolving if the latter is accompanied by cooling; in the contrary case crystals will separate.

(6) In the motion of a conductor in a magnetic field an induction current arises on which the magnetic field acts with a force that opposes the motion. The current that arises in a conductor, owing to a magnet approaching it, repels the latter, and vice versa. It can be seen from this example that Lenz's law is a particular case of the Le Chatelier-Braun principle.

(7) If an electric current passes through the junction of two metals, the junction temperature varies in such a manner that the arising thermo-electric current will tend to diminish the current passed through the junction (the Peltier effect).

It can be seen from all these examples that the Le Chatelier-Braun principle is caused by the stability of a state. In fact, if any primary process whatever were to be further reinforced by a secondary process caused by it, this would lead to completely upsetting the equilibrium of the system. A conductor that is found in a magnetic field and has received an impact, would continue to move further and would moreover accelerate; a magnet slightly pushed away from its coil would continue to move away from it, etc.

The Le Chatelier-Braun principle is not applicable to all systems nor to all possible external disturbances: a preliminary condition is needed, namely a certain degree of stability of the initial state of the system. The Le Chatelier-Braun principle is inapplicable to processes that lead a system to a more stable state, for examples to explosions, to reactions caused by heating, etc.

99. The work of chemical forces in isobaric-isothermal processes is equal to the decrease of Gibbs' thermodynamic potential and is determined by the Gibbs-Helmholtz equation (5.2)

$$W_p = Q_p + T(\partial W/\partial T)_p, \quad (5.2)$$

where Q_p is the heat of reaction. It is known that

$$dZ = SdT - pdV + \sum_i \mu_i dN_i$$

and in isobaric-isothermal processes

$$dZ = \sum_i \mu_i dN_i = dn \sum_i \mu_i v_i,$$

where dn is the number of "individual reactions" determined by a single set of molecules according to the reaction equation. The work

$$W = -dZ = -\Delta n \sum_i \nu_i \mu_i = -\Delta n \sum_i \nu_i (kT \log_e c_i + kT \log_e p + \mu_{oi}(T)).$$

From (6.29)

$$kT \log_e [K_c(p, T)] = -kT \sum_i \nu_i \log_e p - \sum_i \nu_i \mu_{oi}(T),$$

and therefore

$$W = \Delta n kT [\log_e K_c - \sum_i \nu_i \log_e c_i].$$

By determining $(\partial W / \partial T)_p$ from here and substituting in (5.2) we shall find

$$(\partial \log_e K_c / \partial T)_p = -Q_p / RT^2,$$

i.e. the influence of temperature on the quantity K_c and, therefore, also on the equilibrium condition with respect to the chemical reaction, is determined by the heat effect Q_p of this reaction.

100. If the expression for ΔZ given in the problem no. 99

$$\Delta Z = -W = \Delta n kT [\sum_i \nu_i \log_e c_i - \log_e K_c]$$

is differentiated with respect to p for $T = \text{const}$, we shall obtain

$$(\partial \Delta Z / \partial p)_T = -\Delta n kT (\partial \log_e K_c / \partial p)_T.$$

By bearing in mind that $V = (\partial Z / \partial p)_T$, we obtain finally

$$(\partial \log_e K_c / \partial p)_T = -\Delta V / RT,$$

where ΔV is the volume variation of the mixture of reacting substances as a result of the reaction (for the case when $\Delta n k = R$). The influence of pressure on the quantity K_c and, therefore, also on the equilibrium condition is determined by the corresponding volume variation of the system.

101. The reaction of the formation of water-gas occurs without variation of the number of moles. Therefore

$$K_c = K_p = c_{\text{H}_2\text{O}} c_{\text{CO}} / c_{\text{CO}_2} c_{\text{H}_2} = (9.46 \times 9.46) / (0.7 \times 80.38) = 1.591.$$

$$102. \quad \nu_{\text{H}_2} = 1, \quad \nu_{\text{I}_2} = 1, \quad \nu_{\text{HI}} = 2, \quad c_{\text{H}_2} c_{\text{I}_2} / c_{\text{HI}}^2 = K_c = K_p.$$

If x moles of H_2 out of $a = 8.1$ moles, react with the same number of moles of I_2 (out of a total number $b = 2.94$ moles) and $2x$ moles of HI are formed, we have at equilibrium

$$c_{\text{H}_2} = (a - x) / (a + b) = (8.1 - x) / 11.04,$$

$$c_{\text{I}_2} = (b - x) / (a + b) = (2.94 - x) / 11.04,$$

$$c_{\text{HI}} = 2x / (a + b) = 2x / 11.04,$$

and therefore

$$(8.1 - x)(2.94 - x) / 4x^2 = 0.01984,$$

whence $x = 2.82$. The number of moles of HI at equilibrium is $n_{\text{HI}} = 5.64$.

103. We have a two-phase system consisting of different substances (for example, water and kerosene). The entropy of such a system is equal to

$$S = N_1 s_1 + N_2 s_2.$$

The internal parameters of the system are N_1 , N_2 , v_1 , v_2 , u_1 and u_2 . They satisfy the conditions

$$\begin{aligned} N_1 &= \text{const}, & N_2 &= \text{const}, \\ N_1 u_1 + N_2 u_2 &= U = \text{const}, \\ N_1 v_1 + N_2 v_2 &= V = \text{const}. \end{aligned}$$

Thus, of the six parameters, two are independent, for example v_1 and u_1 .

The equilibrium condition will be found from $\delta S = 0$ under the additional conditions

$$\delta N_1 = \delta N_2 = 0, \quad N_1 \delta u_1 + N_2 \delta u_2 = 0, \quad N_1 \delta v_1 + N_2 \delta v_2 = 0.$$

We have $N_1 \delta s_1 + N_2 \delta s_2 = 0$ or

$$\begin{aligned} N_1 T_1^{-1} (\delta u_1 + p_1 \delta v_1) + N_2 T_2^{-1} (\delta u_2 + p_2 \delta v_2) &= 0, \\ N_1 T_1^{-1} (\delta u_1 + p_1 \delta v_1) - N_1 T_2^{-1} (\delta u_1 + p_2 \delta v_1) &= 0 \end{aligned}$$

whence

$$(T_1^{-1} - T_2^{-1}) \delta u_1 + (p_1 T_1^{-1} - p_2 T_2^{-1}) \delta v_1 = 0$$

and

$$T_1 = T_2, \quad p_1 = p_2.$$

No condition is imposed in this case on the chemical potentials, since there can be no exchange of particles in different substances.

104. The number of thermodynamic degrees of freedom is determined by the equation $f = k + 2 - n$.

(a) We have one gaseous phase (vapour), one liquid phase (solution) and two solid phases: $n = 4$; the number of components is equal to the number of chemically independent component parts of the system, H_2O , NaCl and KCl , $k = 3$. Therefore $f = 1$. A system with one degree of freedom is called *monovariant*. Without altering the number of phases of the system, we can vary either its temperature, or pressure, or the concentration of one of the salts of the solution.

(b) $k = 3$, $n = 5$ (the solution, three crystals, water vapour), and therefore $f = k + 2 - n = 0$.

105. The phase rule will not be modified. In fact, if in all phases of the system m components are missing on the whole, then this decreases the number of variables by m , but, at the same time, also the number of equations for the chemical potentials will decrease by the same amount.

106. We have a two-phase system of two volatile liquids and their vapours (for example, water and alcohol in the liquid phase and in vapour form). We shall take the liquid as the first phase and vapour as the second phase.

The behaviour of binary systems is determined by the Gibbs-Duhem equation (6.49):

$$(S''N_2' - S_1'N_2'') dt - (V''N_2' - V_1'N_2'') dp + (N_1''N_2' - N_1'N_2'') d\mu_1 = 0. \quad (6.49)$$

We shall establish by means of this equation a series of properties of binary systems.

(a) Let us find the dependence of pressure on the concentration of any one (for example, the first) component at constant temperature (instead of concentration we shall use the chemical potential which is proportional to the logarithm of concentration). From (6.49) we have

$$\begin{aligned} (\partial p / \partial \mu_1)_T &= (N_1''N_2' - N_1'N_2'') / (V''N_2' - V_1'N_2'') = \\ &= (N_1''N_2'^{-1} - N_1'N_2'^{-1}) / (V''N_2'^{-1} - V_1'N_2'^{-1}). \end{aligned} \quad (1)$$

It can easily be shown that the denominator in this expression is greater than zero; in fact

$$V'' = v_1'' N_1'' + v_2'' N_2''$$

(V'' is the volume of the second phase, v_1'' and v_2'' are the volumes referred to one particle respectively of the first and second component in the second phase), whence

$$V''/N_2'' = v_1'' N_1''/N_2'' + v_2''.$$

Similarly

$$V' = v_1' N_1' + v_2' N_2'$$

and

$$V_1'/N_2' = v_1' N_1'/N_2' + v_2'$$

Therefore

$$V'' N_2''^{-1} - V' N_2'^{-1} = v_1'' N_1'' N_2''^{-1} - v_1' N_1' N_2'^{-1} + v_2'' - v_2' > 0,$$

since $v_1'' \gg v_1'$ and $v_2'' \gg v_2'$ (for temperatures far removed from the critical temperatures). Therefore if $N_1''/N_2'' > N_1'/N_2'$ (the ratio of the number of molecules of the first component to the number of molecules of the second component in the vapour is larger than in the liquid, i.e. the vapour is richer of the first component than the liquid), then $(dp/d\mu_1)_T > 0$.

Thus we establish that *the vapour pressure of the mixture increases* ($(dp/d\mu_1)_T > 0$) *for an increase of the component (the first one) of which the gaseous phase is richer, or else that the more volatile component of a binary mixture is the one an addition of which increases the vapour tension of the mixture.* (Konovalov's first rule). It follows

from this rule that, if we increase the concentration of a component in the liquid phase, it will also increase in the gaseous phase; in fact, it can be seen from $N_1''/N_2'' > N_1'/N_2'$ that, for the inequality to be retained, an increase of N_1' must be accompanied by an increase of N_1'' . Therefore both phase-equilibrium curves as functions of concentration must either simultaneously increase or simultaneously decrease, which is found in agreement with experiment.

The properties of binary systems are represented on so-called diagrams of state, on which the concentration is plotted on the axis of the abscissae, and temperature or pressure is plotted on the axis of the ordinates. The origin of the coordinates (the point 0) corresponds to the pure substance of the second component ($c_2 = 1$ and $c_1 = 0$), while the point A corresponds to the pure substance of the first component ($c_1 = 1$, $c_2 = 0$; $c_1 + c_2 = 1$).

The dependence of p on c_1 is shown on the c, p diagram and, in the majority of cases has the form of a cigar (Fig. 61); for one and the same vapour tension p_1 , liquid and vapour have different composition— c_1' and c_1'' . In accordance with Konovalov's first rule, an increase of concentration in the liquid phase (moving from A to B) increases the concentration in the vapour also (A' moves to B').

(b) When pressure is maintained constant the equilibrium temperature of binary phases is completely determined by the composition of one of them. The equation

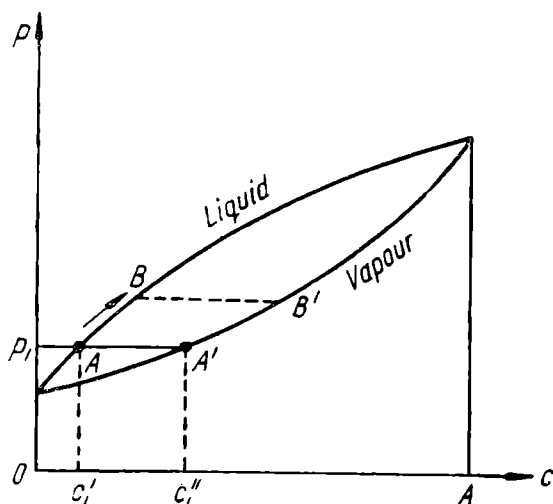


FIG. 61.

(6.49) enables us to find the dependence of the boiling temperature of a mixture on the concentration at constant pressure:

$$\begin{aligned} (\partial T / \partial \mu_1)_p &= (N_1' N_2'' - N_1'' N_2') / (S'' N_2' - S' N_2'') = \\ &= (N_1'' N_2''^{-1} - N_1' N_2'^{-1}) / (S'' N_2''^{-1} - S' N_2'^{-1}). \end{aligned} \quad (2)$$

The denominator of the right-hand side of this expression, just as that of the expression (1), is larger than zero, and therefore for $N_1'/N_2' > N_1''/N_2''$ we have

$$(\partial T / \partial \mu_1)_p < 0,$$

i.e. an addition of the more volatile component (the component of which the vapour is richer than the liquid; in our case the first component) lowers the boiling temperature. The dependence of the boiling temperature of a binary system on concentration

at constant pressure is represented on a c, T diagram (Fig. 62).

(c) It follows from the fundamental equation for binary systems (6.49) that, if a binary mixture is such that the curve of vapour tension (or the curve of the boiling temperature) of this system passes through a maximum or through a minimum as the concentration varies (Figs. 63 and 64), then the composition of the vapour at these points is equal to the composition of the liquid at the same points (Konovalov's second rule). In fact, from the equation (1) for

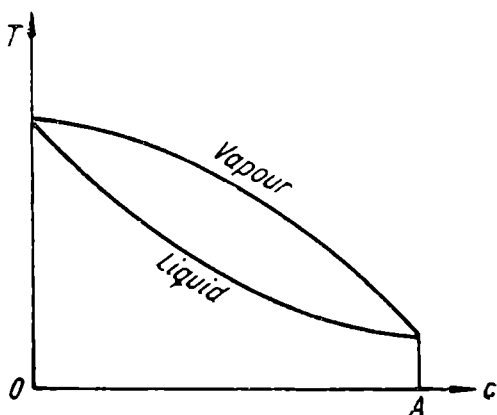


FIG. 62.

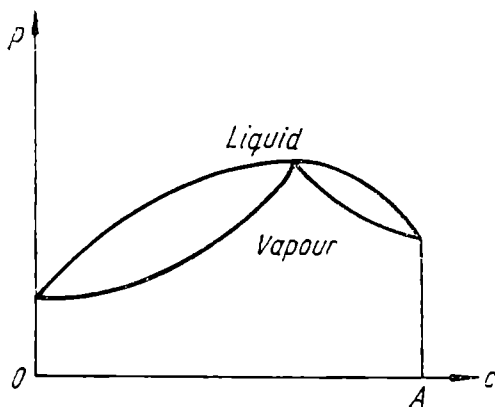


FIG. 63.

$$(\partial p / \partial \mu_1)_T = 0$$

we obtain $N_1'/N_2' = N_1''/N_2''$, i.e. the composition of the phases is the same.

Konovalov's rules have great importance in the engineering of separation of mixtures, for example by distillation.

At extremum points no component of the mixture can be separated by distillation, since in such a case the components are found in the same composition both in the liquid and the vapour. Chemists thought at first that at these points a binary system is not a mixture but a chemical compound. This is, however, incorrect since the composition of such a mixture depends on temperature. We can, however, not at the extrema, but on the ascending or descending sections of the

curves where the composition of the phases is not the same, isolate by boiling (distillation) one of the components of the mixture, i.e. separate the mixture; by prolonged boiling of the liquid the more volatile component will be vaporized and its quantity in the liquid will decrease, since at such points the components pass to vapour not in the same ratios.

107. Surface tension, by modifying the condition of mechanical equilibrium, leads to the fact that the saturated vapour pressure at a given temperature has different values on drops of different dimensions.

Let us find the dependence of the saturated vapour pressure on a drop upon the value of its radius. Let a drop of liquid (the first phase) of radius r be in equilibrium with its vapour (the second phase). We have for equilibrium

$$\mu_1(p_1, T) = \mu_2(p_2, T). \quad (1)$$

For a plane surface

$$\mu_1(p, T) = \mu_2(p, T). \quad (2)$$

As a consequence of the small compressibility of liquid we can write

$$\begin{aligned} \mu_1(p_1, T) - \mu_1(p, T) = \\ (\partial\mu_1/\partial p)(p_1 - p) = v_1(2\sigma/r). \end{aligned} \quad (3)$$

By assuming vapour to be an ideal gas and knowing the chemical potential of such a gas, we have

$$\mu_2(p_2, T) - \mu_2(p, T) = kT \log_e(p_2/p). \quad (4)$$

Since the left-hand sides of the equations (3) and (4) are equal, then, by equating the right-hand sides, we obtain

$$p_2 = p \exp(2v_1\sigma/rkT). \quad (5)$$

It can be seen from this formula that the saturated vapour pressure of small drops is larger than that of large drops.

108. If drops in vapour acquire an electric charge, they begin to increase, though being very small, and not only in oversaturated vapour but also in vapour that has not reached saturation. In fact let a drop of radius r acquire an ion with charge e and radius a ; at equilibrium the ion is concentrated at the centre of the drop. If such a drop begins to increase, this will lead to a decrease of the free energy of the electric field and, therefore, of the thermodynamic potential.

Similarly to (7.16) the expression for ΔF for the forming of a drop of liquid about an ion will be equal to

$$\Delta F = [4\pi r^3/3v_2](\mu_2 - \mu_1) + 3\pi\sigma r^2 + \Delta F_e, \quad (1)$$

where ΔF_e is the variation of free energy of the electric field for the forming of a charged drop (μ_2 is the chemical potential of the drop). It is equal to the difference between the energy of the field generated by the ion that is found at the centre of the drop and the energy of the field of a free ion:

$$\begin{aligned} \Delta F_e &= \epsilon(8\pi)^{-1} \int_a^r E_1^2 dV + (8\pi)^{-1} \int_r^\infty E^2 dV - (8\pi)^{-1} \int_a^\infty E^2 dV = \\ &= \epsilon(8\pi)^{-1} \int_a^r E_1^2 dV - (8\pi)^{-1} \int_a^r E^2 dV = \\ &= (e^2/2) \int_a^r (\epsilon r^2)^{-1} dr - (e^2/2) \int_a^r r^{-2} dr = e^2(2r)^{-1}(1 - \epsilon^{-1}) + e^2(2a)^{-1}(\epsilon^{-1} - 1) \end{aligned}$$

(E_1 is the field intensity in the drop, E is the field intensity outside the drop, and ϵ the permittivity of the drop).

Thus

$$\Delta F = 4\pi r^3(3v_2)^{-1}(\mu_2 - \mu_1) + 4\pi\sigma r^2 + (e^2/2)(1 - \epsilon^{-1})(r^{-1} - a^{-1}). \quad (2)$$

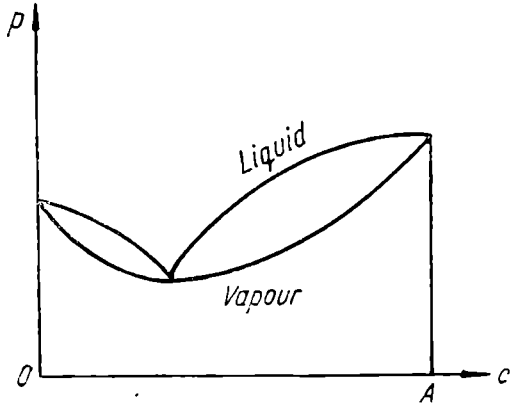


FIG. 64.

The latter term is (2) is negative, being the larger in modulus the larger the drop (the second phase). Consequently, with an increase of the drop, the value of ΔF will decrease owing to the electric charge and, if in the absence of charge a drop of whatever dimensions always evaporated for $\mu_2 > \mu_1$, now even a small drop (for $\mu_2 > \mu_1$) can lead by its growing to a decrease of ΔF and can thus increase and cause condensation.

This phenomenon is used in Wilson's chamber for detecting traces of fast ionizing particles: the formation of ions on the path followed by a particle cause vapour condensation on them, which makes the trace of the particle visible.

109. In the case of electrolytes when the dissolved substances are ionized, their adsorption in a surface layer leads to the electrification of the latter. If e_i is the excess of concentration of charge of the i -th ions in the surface layer and φ is the electric potential of the layer then the variation of its free energy for an increase of the surface Σ and of the quantities e_i is equal to

$$dF = \sigma d\Sigma + \sum_{(i)} \varphi de_i = \sigma d\Sigma + \varphi de,$$

where $e = \sum_{(i)} e_i$.

From this we obtain, similarly to (7.20)

$$(\partial\sigma/\partial\varphi)_\Sigma = -(\partial e/\partial\Sigma)_\varphi. \quad (1)$$

This equation determines the relation between the electric charge per unit surface of solution of the electrolyte and its surface tension.

The quantity

$$q = (\partial e/\partial\Sigma)_\varphi$$

is the excess of concentration of charges of all ions in the surface layer on its unit surface, i.e. the charge of the unit surface. We obtain from the equation (1)

$$q = -(\partial\sigma/\partial\varphi)_\Sigma. \quad (2)$$

Thus, in the case of an electrolyte, together with Gibbs' equation (7.22) characterizing the adsorption of substance on the boundary surface of the electrolyte we must consider the equation (2).

110.

$$dp/dT = \lambda T^{-1}(V_2 - V_1)^{-1}, \quad (1)$$

where V_2 is the volume of a mole of vapour, and V_1 is the volume of a mole of liquid. Far away from the critical point we have $V_2 \gg V_1$. By assuming that saturated vapours satisfy Clapeyron's equation of state, the equation (1) assumes the form

$$dp/dT = \lambda p/RT^2,$$

whence

$$p = \text{const.} \exp(-\lambda/RT).$$

111.

$$\lambda = (dp/dT)(V_2 - V_1)/T,$$

where V_1 and V_2 are the molar volumes of liquid and vapour respectively. Since $V_2 \gg V_1$, then, by applying to the vapour the law of the gaseous state, we shall obtain $\lambda = (dp/dT)RT^2/p = 4.35 \times 2 \times 387^2/88.88 = 14,550$ cal/mole.

112. To determine the pressure under which water boils at $T = 95 + 273 = 368^\circ\text{K}$ means to find the saturated-vapour pressure at this temperature. According to the problem no. 106, $p = C \exp(-\lambda/RT)$. For $T = 373^\circ\text{K}$ the vapour pressure p_1 is equal to 760 mm Hg, $p_1 = C \exp(-\lambda/RT_1)$, whence $C = p_1 \exp(\lambda/RT_1)$ and $p = p_1 \exp[-\lambda R^{-1}(T^{-1} - T_1^{-1})] = 760 \exp[-(539 \times 18/2)(368^{-1} - 373^{-1})] = 636$ mm Hg.

113. For a superconductor in a field H

$$dZ_s = -SdT - MdH.$$

By substituting in here $M = -H/4\pi$ and integrating we shall have

$$z_s(H) = z_s(0) + (8\pi)^{-1}H^2.$$

Along the curve of the critical field where n and s are found in equilibrium, the specific thermodynamic potentials in the two states are the same, and therefore

$$z_n = z_s = z_s(0) + (8\pi)^{-1}H_c^2$$

$$z_n - z_s(0) = (8\pi)^{-1}H_c^2$$

and

$$s_n - s_s = -(H_c/4\pi)(dH_c/dT), \quad (1)$$

where s_s is taken in the absence of the field.

The difference of the thermal capacities is

$$\Delta c = c_s - c_n = Td(s_s - s_n)/dT = (TH_c/4\pi)(d^2H_c/dT^2) + (T/4\pi)(dH_c/dT)^2. \quad (2)$$

For $T = T_c$ the critical field $H_c = 0$, and we obtain from (1) $S_n = S_s$ and from (2) Rutgers' formula (8.14):

$$\Delta c = (T_c/4\pi)(dH_c/dT)^2.$$

For

$$H_c(T) = H_0[1 - (T/T_c)^2]$$

and from (1) and (2) we obtain

$$s_n - s_s = (H_0^2 T / 2\pi T_c^2)[1 - (T/T_c)^2]$$

and

$$c_n - c_s = (H_0^2 T / 2\pi T_c^2)[1 - 3(T/T_c)^2].$$

114. Jüsti and Laue's error is based on the assumption of the existence of superheated or supercooled phases in phase transitions of the second kind (similarly to that which occurs in phase transitions of the first kind), which is not observed in reality. Therefore the right-hand branch (on the right of the transition point) of the Z_1 curve or its left-hand branch on Fig. 35b (page 193) do not exist.

115. From $(p + aV^{-2})(V - b) = RT$ we have

$$(\partial V / \partial T)_p = R(V - b) / [RT - 2aV^{-3}(V - b)^2] \quad (1)$$

and

$$(\partial V / \partial p)_T = -(V - b)^2 / [RT - 2aV^{-3}(V - b)^2]. \quad (2)$$

By substituting in (1) and (2) the critical values of V and T : $V_{cr} = 3b$ and $T_{cr} = (8/27)(a/Rb)$, we shall obtain

$$(\partial V / \partial T)_{p_{cr}, T_{cr}} = (\partial V / \partial p)_{p_{cr}, T_{cr}} = \infty.$$

116. Integration of the equation (9.1) leads to the solution

$$W = -T \int Q T^{-2} dT + IT, \quad (1)$$

where I is a thermodynamically-undetermined quantity.

Let us expand the heat effect Q in a power series

$$Q = Q_0 + \alpha T + \beta T^2 + \gamma T^3 + \dots,$$

whence

$$dQ/dT = \alpha + 2\beta T + 3\gamma T^2 + \dots$$

By Nernst's theorem $\lim dQ/dT = 0$ for $T \rightarrow 0$ and therefore $\alpha = 0$ and $Q = Q_0 + \beta T^2 + \gamma T^3$. By substituting this in (1) we shall obtain

$$W = Q_0 - \beta T^2 - (1/2)\gamma T^3 - \dots + IT,$$

whence

$$dW/dT = -2\beta T - (3/2)\gamma T^2 - \dots + I.$$

By Nernst's theorem $\lim_{T \rightarrow 0} dW/dT = 0$, and therefore $I = 0$. Thus

$$W = -T \int Q T^{-2} dT \quad (2)$$

and

$$\left. \begin{aligned} Q &= Q_0 + \beta T^2 + \gamma T^3 + \dots \\ W &= Q_0 - \beta T^2 - (1/2)\gamma T^3 + \dots \end{aligned} \right\} \quad (3)$$

117. In the general case

$$dF = -SdT - \sum_i A_i da_i,$$

whence

$$(\partial A_i / \partial T)_{a_i} = (\partial S / \partial a_i)_{T, a_j}.$$

For $T \rightarrow 0$ the entropy is independent of the parameters of state, i.e.

$$(\partial S / \partial a_i)_{T, a_j} \rightarrow 0 \text{ for } T \rightarrow 0,$$

and therefore the generalized forces A_i (pressure, surface tension, e.m.f. etc.) are independent of temperature for $T \rightarrow 0$.

118. By the formulae (3) of the solution of the problem no. 116 the affinity is

$$W = Q_0 - \beta T^2 = 50.4 - 3.69 \times 10^{-4} T^2.$$

At the transition point the two sulphur modifications are found in equilibrium ($\mu_1 = \mu_2$ or $Z_1 = Z_2$) and $W = Z_1 - Z_2 = 0$, and therefore the transition temperature is found from the equation $50.4 - 3.69 \times 10^{-4} T_0^2 = 0$ and is equal to $T_0 = 369.5^\circ\text{K}$ (the value found experimentally is $T_0 = 368.4^\circ\text{K}$). At the temperature T_0 there is no tendency to transition; below this temperature rhombic sulphur is stable and therefore monoclinic sulphur will, under the influence of chemical-affinity forces, transform spontaneously to rhombic sulphur.

119. The level differences arising in vessels filled with liquid and joined by a capillary, when a temperature difference is maintained in them, is called the *thermomechanical effect* and, in ordinary liquids, is an irreversible process similar to the thermoelectric effect (at the junction of two different conductors with different temperatures there arises a thermo-e.m.f.; see § 49). A thermomechanical effect of such kind exists also in He-II, but in this case it is masked by another reversible effect, considerably exceeding the former and specific for He-II (the latter is also called thermomechanical effect).

As has already been said in the statement of the problem, He-II behaves as the "mixture" of two liquids—a superfluid (s) and a normal one (n)†. When the temperature in communicating vessels with He-II is the same, the "concentrations" of the superfluid and normal components are the same in both vessels. If, however, the temperature in one of the vessels is increased, then the concentration of the superfluid (normal) component in it decreases (increases), since a portion of the s -component passes in this connexion to normal. The difference arising in the concentrations of components in the different vessels will be equalized: the s -component will flow to the warmer vessel, and the normal component vice versa. Owing to the fact that the s -component can freely flow through the capillary the equality of its concentrations in the two vessels is rapidly established, whereas the equalizing of the concentrations of the n -component in the vessels will occur considerably more slowly owing to friction. As a result, liquid rises in the warmer vessel and generates a pressure difference Δp (Fig. 65).

† Of course, such a description of He-II, just as any classical model of quantum phenomena, is merely a convenient method for expressing the behaviour of a quantum liquid, such as He-II is. No such separation of the particles of helium into "superfluid" and "normal" ones exists.

We shall find the relation between Δp and the value of ΔT , that gives rise to it, from the condition of the "chemical equilibrium" of helium in the vessels as is established as a result of "exchange" of the s -component. As is known (see page 131), such an equilibrium occurs for equal chemical potentials (which we shall refer to lg of helium)

$$\mu(p_1, T_1) = \mu(p_2, T_2) \quad (1)$$

(p_1, T_1 and p_2, T_2 are the pressure and temperature in the first and second vessels).

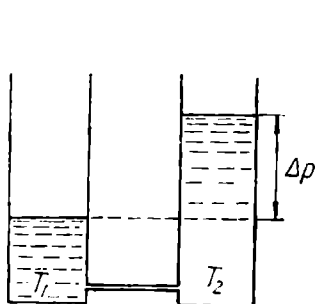


FIG. 65.

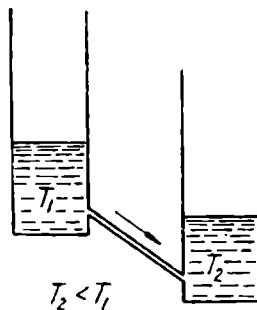


FIG. 66.

Since for equal temperatures in the vessels the values of pressure in them are the same at one and the same height, then for a small temperature difference $\Delta T = T_2 - T_1$ the pressure difference $\Delta p = p_2 - p_1$ will also be small. Therefore by expanding $\mu(p_2, T_2)$ in a power series with respect to ΔT and Δp , we obtain from (1)

$$\mu(p_2, T_2) - \mu(p_1, T_1) = (\partial\mu/\partial p)_T \Delta p + (\partial\mu/\partial T)_p \Delta T = 0$$

or

$$v\Delta p - s\Delta T = 0$$

(v and s are the volume and entropy of lg He-II), whence

$$\Delta p/\Delta T = s/v,$$

or

$$\Delta p/\Delta T = \rho s, \quad (2)$$

where ρ is the density of He-II at the given temperature.

Since $\rho s > 0$, then $\Delta p/\Delta T > 0$, and therefore for $\Delta T > 0$ the pressure difference is positive, i.e. liquid rises in the warmer vessel.

The formula (2) was firstly established in 1939 by H. London using the method of cycles and was quantitatively confirmed two years later by P. L. Kapitza's experiments, while L. D. Landau obtained it by the method of thermodynamic potentials.

The thermomechanical effect is reversible, i.e. if the temperature difference in He-II causes the arising of a pressure difference, then a pressure difference will cause a corresponding temperature difference. This *mechanocaloric effect* in He-II was investigated in 1939 when it was revealed that the flowing of He-II through a capillary from a higher to a lower level is accompanied by the arising of a temperature difference in the vessels (Fig. 66).

Quantitatively the dependence of ΔT on Δp in the mechanocaloric effect is determined by the same relation (2) which we shall now write in the form

$$\Delta T/\Delta p = 1/\rho s. \quad (3)$$

It can be seen from this formula that in the lower vessel (with pressure $p_2 < p_1$, where p_1 is the pressure in the upper vessel), into which He-II flows, the temperature is lowered: for $\Delta p = p_2 - p_1 < 0$ the difference $\Delta T = T_2 - T_1$ is negative and $T_2 < T_1$.

This result is due to the same property of the superfluid component of He-II of flowing freely through a capillary: the entropy of this component is equal to zero, and therefore, by Nernst's theorem, it "is found" at the absolute zero temperature.

120. If in the expression for the density of entropy flow in a thermally inhomogeneous conductor with current (see (11.18)) we substitute the value of I from (11.22) we shall obtain

$$S = -(\Pi/T)j - (\kappa/T) \text{grad } T.$$

Here the first term determines the entropy flow caused by the motion of charges (electric current) and the second term is caused by thermal conductivity. Let us denote the value of the first term by $-S_j$. Then $S_j = (\Pi/T)j$ and $\Pi = (T/j)S_j$. By using (11.24) and (11.28) we obtain

$$\alpha = (1/j)S_j \quad \text{and} \quad \tau = (T/j) (\partial S_j / \partial T).$$

Similarly

$$\kappa = (T/|\nabla T|) S_{\nabla T}.$$

It can be seen from this that thermoelectric phenomena are connected with the transport of entropy by current, which explains their known "reversibility" (see the discussion on the sign of Thomson's heat in § 49).

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